



PHILOSOPHICAL
TRANSACTIONS
OF THE
ROYAL SOCIETY OF LONDON.

SERIES A

CONTAINING PAPERS OF A MATHEMATICAL OR PHYSICAL CHARACTER.

VOL. 193.

LONDON:

PRINTED BY HARRISON AND SONS, ST. MARTIN'S LANE, W.C.,

Printers in Ordinary to Her Majesty.

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PHILOSOPHICAL
TRANSACTIONS

ROYAL SOCIETY OF LONDON

VOLUME A

CONTAINING THE PROCEEDINGS OF THE SOCIETY

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PRINTED

BY J. JOHNSON, STATIONER, AND PRINTER, 15, N. B. STREET, LONDON.

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ADVERTISEMENT.

THE Committee appointed by the *Royal Society* to direct the publication of the *Philosophical Transactions* take this opportunity to acquaint the public that it fully appears, as well from the Council-books and Journals of the Society as from repeated declarations which have been made in several former *Transactions*, that the printing of them was always, from time to time, the single act of the respective Secretaries till the Forty-seventh Volume; the Society, as a Body, never interesting themselves any further in their publication than by occasionally recommending the revival of them to some of their Secretaries, when, from the particular circumstances of their affairs, the *Transactions* had happened for any length of time to be intermitted. And this seems principally to have been done with a view to satisfy the public that their usual meetings were then continued, for the improvement of knowledge and benefit of mankind: the great ends of their first institution by the Royal Charters, and which they have ever since steadily pursued.

But the Society being of late years greatly enlarged, and their communications more numerous, it was thought advisable that a Committee of their members should be appointed to reconsider the papers read before them, and select out of them such as they should judge most proper for publication in the future *Transactions*; which was accordingly done upon the 26th of March, 1752. And the grounds of their choice are, and will continue to be, the importance and singularity of the subjects, or the advantageous manner of treating them; without pretending to answer for the certainty of the facts, or propriety of the reasonings contained in the several papers so published, which must still rest on the credit or judgment of their respective authors.

It is likewise necessary on this occasion to remark, that it is an established rule of the Society, to which they will always adhere, never to give their opinion, as a Body,

upon any subject, either of Nature or Art, that comes before them. And therefore the thanks, which are frequently proposed from the Chair, to be given to the authors of such papers as are read at their accustomed meetings, or to the persons through whose hands they received them, are to be considered in no other light than as a matter of civility, in return for the respect shown to the Society by those communications. The like also is to be said with regard to the several projects, inventions, and curiosities of various kinds, which are often exhibited to the Society ; the authors whereof, or those who exhibit them, frequently take the liberty to report, and even to certify in the public newspapers, that they have met with the highest applause and approbation. And therefore it is hoped that no regard will hereafter be paid to such reports and public notices ; which in some instances have been too lightly credited, to the dishonour of the Society.

1899.

LIST OF INSTITUTIONS ENTITLED TO RECEIVE THE PHILOSOPHICAL TRANSACTIONS OR
PROCEEDINGS OF THE ROYAL SOCIETY.

Institutions marked A are entitled to receive Philosophical Transactions, Series A, and Proceedings.

"	"	B	"	"	"	"	Series B, and Proceedings.
"	"	AB	"	"	"	"	Series A and B, and Proceedings.
"	"	P	"	"	"	"	Proceedings only.

America (Central).

Mexico.

p. Sociedad Científica "Antonio Alzate."

America (North). (See UNITED STATES and CANADA.)**America (South).**

Buenos Ayres.

AB. Museo Nacional.

Caracas.

B. University Library.

Cordova.

AB. Academia Nacional de Ciencias.

Demerara.

p. Royal Agricultural and Commercial
Society, British Guiana.

La Plata.

B. Museo de La Plata.

Rio de Janeiro.

p. Observatorio.

Australia.

Adelaide.

p. Royal Society of South Australia.

Brisbane.

p. Royal Society of Queensland.

Melbourne.

p. Observatory.

p. Royal Society of Victoria.

AB. University Library.

Sydney.

p. Australian Museum.

p. Geological Survey.

p. Linnean Society of New South Wales.

AB. Royal Society of New South Wales.

AB. University Library.

Austria.

Agram.

p. Jugoslavenska Akademija Znanosti i Um-
jetnosti.

p. Societas Historico-Naturalis Croatia.

VOL. CXCHL.—A.

Austria (continued).

Brünn.

AB. Naturforschender Verein.

Graz.

AB. Naturwissenschaftlicher Verein für Steier-
mark.

Innsbruck.

AB. Das Ferdinandeum.

p. Naturwissenschaftlich - Medicinischer
Verein.

Prague.

AB. Königliche Böhmisches Gesellschaft der
Wissenschaften.

Trieste.

B. Museo di Storia Naturale.

p. Società Adriatica di Scienze Naturali.

Vienna.

p. Anthropologische Gesellschaft.

AB. Kaiserliche Akademie der Wissenschaften.

p. K.K. Geographische Gesellschaft.

AB. K.K. Geologische Reichsanstalt.

B. K.K. Naturhistorisches Hof-Museum.

B. K.K. Zoologisch-Botanische Gesellschaft.

p. Oesterreichische Gesellschaft für Meteoro-
logie.

A. Von Kuffner'sche Sternwarte.

Belgium.

Brussels.

B. Académie Royale de Médecine.

AB. Académie Royale des Sciences.

B. Musée Royal d'Histoire Naturelle de
Belgique.

p. Observatoire Royal.

p. Société Belge de Géologie, de Paléonto-
logie, et d'Hydrologie.

p. Société Malacologique de Belgique.

Ghent.

AB. Université.

Belgium (continued).**Liège.**

- AB. Société des Sciences.
- p. Société Géologique de Belgique.

Louvain.

- B. Laboratoire de Microscopie et de Biologie Cellulaire
- AB. Université.

Canada.**Fredericton, N.B.**

- p. University of New Brunswick.

Halifax, N.S.

- p. Nova Scotian Institute of Science.

Hamilton.

- p. Hamilton Association.

Montreal.

- AB. McGill University.
- p. Natural History Society.

Ottawa.

- AB. Geological Survey of Canada.
- AB. Royal Society of Canada.

St. John, N.B.

- p. Natural History Society.

Toronto.

- p. Astronomical and Physical Society.
- p. Canadian Institute.
- AB. University.

Windsor, N.S.

- p. King's College Library.

Cape of Good Hope.

- A. Observatory.
- AB. South African Library.

Ceylon.**Colombo.**

- A. Museum.

China.**Shanghai.**

- p. China Branch of the Royal Asiatic Society.

Denmark.**Copenhagen.**

- AB. Kongelige Danske Videnskabernes Selskab.

Egypt.**Alexandria.**

- AB. Bibliothèque Municipale.

England and Wales.**Aberystwith.**

- AB. University College.

Bangor.

- AB. University College of North Wales.

Birmingham.

- AB. Free Central Library.
- AB. Mason College.
- p. Philosophical Society.

England and Wales (continued).**Bolton.**

- p. Public Library.

Bristol.

- p. Merchant Venturers' School.
- AB. University College.

Cambridge.

- AB. Philosophical Society.
- p. Union Society.

Cooper's Hill.

- AB. Royal Indian Engineering College.

Dudley.

- p. Dudley and Midland Geological and Scientific Society.

Essex.

- p. Essex Field Club.

Falmouth.

- p. Royal Cornwall Polytechnic Society.

Greenwich.

- A. Royal Observatory.

Kew.

- B. Royal Gardens.

Leeds.

- p. Philosophical Society.
- AB. Yorkshire College.

Liverpool.

- AB. Free Public Library.
- p. Literary and Philosophical Society.
- A. Observatory.
- AB. University College.

London.

- AB. Admiralty.
- p. Anthropological Institute.
- AB. British Museum (Nat. Hist.).
- AB. Chemical Society.
- A. City and Guilds of London Institute.
- p. "Electrician," Editor of the.
- B. Entomological Society.
- AB. Geological Society.
- AB. Geological Survey of Great Britain.
- p. Geologists' Association.
- AB. Guildhall Library.
- A. Institution of Civil Engineers.
- p. Institution of Electrical Engineers.
- A. Institution of Mechanical Engineers.
- A. Institution of Naval Architects.
- p. Iron and Steel Institute.
- AB. King's College.
- B. Linnean Society.
- AB. London Institution.
- p. London Library.
- A. Mathematical Society.
- p. Meteorological Office.
- p. Odontological Society.

England and Wales (continued).**London (continued).**

- p.* Pharmaceutical Society.
- p.* Physical Society.
- p.* Quekett Microscopical Club.
- p.* Royal Agricultural Society.
- A.* Royal Astronomical Society.
- B.* Royal College of Physicians.
- B.* Royal College of Surgeons.
- p.* Royal Engineers (for Libraries abroad, six copies).
- AB.* Royal Engineers. Head Quarters Library.
- p.* Royal Geographical Society.
- p.* Royal Horticultural Society.
- p.* Royal Institute of British Architects.
- AB.* Royal Institution of Great Britain.
- B.* Royal Medical and Chirurgical Society.
- p.* Royal Meteorological Society.
- p.* Royal Microscopical Society.
- p.* Royal Statistical Society.
- AB.* Royal United Service Institution.
- AB.* Society of Arts.
- p.* Society of Biblical Archaeology.
- p.* Society of Chemical Industry (London Section).
- p.* Standard Weights and Measures Department.
- AB.* The Queen's Library.
- AB.* The War Office.
- AB.* University College.
- p.* Victoria Institute.
- B.* Zoological Society.

Manchester.

- AB.* Free Library.
- AB.* Literary and Philosophical Society.
- p.* Geological Society.
- AB.* Owens College.

Netley.

- p.* Royal Victoria Hospital.

Newcastle.

- AB.* Free Library.
- p.* North of England Institute of Mining and Mechanical Engineers.
- p.* Society of Chemical Industry (Newcastle Section).

Norwich.

- p.* Norfolk and Norwich Literary Institution.

Nottingham.

- AB.* Free Public Library.

Oxford.

- p.* Ashmolean Society.
- AB.* Radcliffe Library.
- A.* Radcliffe Observatory.

England and Wales (continued).**Penzance.**

- p.* Geological Society of Cornwall.

Plymouth.

- B.* Marine Biological Association.
- p.* Plymouth Institution.

Richmond.

- A.* "Kew" Observatory.

Salford.

- p.* Royal Museum and Library.

Stonyhurst.

- p.* The College.

Swansea.

- AB.* Royal Institution.

Woolwich.

- AB.* Royal Artillery Library.

Finland.**Helsingfors.**

- p.* Societas pro Fauna et Flora Fennica.
- AB.* Société des Sciences.

France.**Bordeaux.**

- p.* Académie des Sciences.
- p.* Faculté des Sciences.
- p.* Société de Médecine et de Chirurgie.
- p.* Société des Sciences Physiques et Naturelles.

Caen.

- p.* Société Linnéenne de Normandie.

Cherbourg.

- p.* Société des Sciences Naturelles.

Dijon.

- p.* Académie des Sciences.

Lille.

- p.* Faculté des Sciences.

Lyons.

- AB.* Académie des Sciences, Belles-Lettres et Arts.
- AB.* Université.

Marseilles.

- AB.* Faculté des Sciences.

Montpellier.

- AB.* Académie des Sciences et Lettres.
- B.* Faculté de Médecine.

Nantes.

- p.* Société des Sciences Naturelles de l'Ouest de la France.

Paris.

- AB.* Académie des Sciences de l'Institut.
- p.* Association Française pour l'Avancement des Sciences.
- p.* Bureau des Longitudes.
- A.* Bureau International des Poids et Mesures.
- p.* Commission des Annales des Ponts et Chaussées.
- p.* Conservatoire des Arts et Métiers.

France (continued).

Paris (continued).

- p.* Cosmos (M. L'ABBÉ VALETTE).
- AB.* Dépôt de la Marine.
- AB.* École des Mines.
- AB.* École Normale Supérieure.
- AB.* École Polytechnique.
- AB.* Faculté des Sciences de la Sorbonne.
- B.* Institut Pasteur.
- AB.* Jardin des Plantes.
- p.* L'Électricien.
- A.* L'Observatoire.
- p.* Revue Scientifique (Mons. H. DE VABIGNY).
- p.* Société de Biologie.
- AB.* Société d'Encouragement pour l'Industrie Nationale.
- AB.* Société de Géographie.
- p.* Société de Physique.
- B.* Société Entomologique.
- AB.* Société Géologique.
- p.* Société Mathématique.
- p.* Société Météorologique de France.

Toulouse.

- AB.* Académie des Sciences.
- A.* Faculté des Sciences.

Germany.

Berlin.

- A.* Deutsche Chemische Gesellschaft.
- A.* Die Sternwarte.
- p.* Gesellschaft für Erdkunde.
- AB.* Königliche Preussische Akademie der Wissenschaften.
- A.* Physikalische Gesellschaft.

Bonn.

- AB.* Universität.

Bremen.

- p.* Naturwissenschaftlicher Verein.

Breslau.

- p.* Schlesische Gesellschaft für Vaterländische Kultur.

Brunswick.

- p.* Verein für Naturwissenschaft.

Carlsruhe. See Karlsruhe.

Charlottenburg.

- A.* Physikalisch-Technische Reichsanstalt.

Danzig.

- AB.* Naturforschende Gesellschaft.

Dresden.

- p.* Verein für Erdkunde.

Emden.

- p.* Naturforschende Gesellschaft.

Erlangen.

- AB.* Physikalisch-Medicinische Societät.

Germany (continued).

Frankfurt-am-Main.

- AB.* Senckenbergische Naturforschende Gesellschaft.

- p.* Zoologische Gesellschaft.

Frankfurt-am-Oder.

- p.* Naturwissenschaftlicher Verein.

Freiburg-im-Breisgau.

- AB.* Universität.

Giessen.

- AB.* Grossherzogliche Universität.

Görlitz.

- p.* Naturforschende Gesellschaft.

Göttingen.

- AB.* Königliche Gesellschaft der Wissenschaften.

Halle.

- AB.* Kaiserliche Leopoldino - Carolinische Deutsche Akademie der Naturforscher.

- p.* Naturwissenschaftlicher Verein für Sachsen und Thüringen.

Hamburg.

- p.* Naturhistorisches Museum.

- AB.* Naturwissenschaftlicher Verein.

Heidelberg.

- p.* Naturhistorisch-Medizinischer Verein.

- AB.* Universität.

Jena.

- AB.* Medicinisch-Naturwissenschaftliche Gesellschaft.

Karlsruhe.

- A.* Grossherzogliche Sternwarte.

- p.* Technische Hochschule.

Kiel.

- p.* Naturwissenschaftlicher Verein für Schleswig-Holstein.

- A.* Sternwarte.

- AB.* Universität.

Königsberg.

- AB.* Königliche Physikalisch - Ökonomische Gesellschaft.

Leipsic.

- p.* Annalen der Physik und Chemie.

- AB.* Königliche Sächsische Gesellschaft der Wissenschaften.

Magdeburg.

- p.* Naturwissenschaftlicher Verein.

Marburg.

- AB.* Universität.

Munich.

- AB.* Königliche Bayerische Akademie der Wissenschaften.

- p.* Zeitschrift für Biologie.

Germany (continued).

Münster.

- AB. Königliche Theologische und Philosophische Akademie.

Potsdam.

- A. Astrophysikalisches Observatorium.

Rostock.

- AB. Universität.

Strasburg.

- AB. Universität.

Tübingen.

- AB. Universität.

Würzburg.

- AB. Physikalisch-Medicinische Gesellschaft.

Greece.

Athens.

- A. National Observatory.

Holland. (See NETHERLANDS.)

Hungary.

Buda-pest.

- p. Königl. Ungarische Geologische Anstalt.
AB. Á Magyar Tudós Társaság. Die Ungarische Akademie der Wissenschaften.

Hermannstadt.

- p. Siebenbürgischer Verein für die Naturwissenschaften.

Klausenburg.

- AB. Az Erdélyi Muzem. Das Siebenbürgische Museum.

Schemnitz.

- p. K. Ungarische Berg- und Forst-Akademie.

India.

Bombay.

- AB. Elphinstone College.
p. Royal Asiatic Society (Bombay Branch).

Calcutta.

- AB. Asiatic Society of Bengal.
AB. Geological Museum.
p. Great Trigonometrical Survey of India.
AB. Indian Museum.
p. The Meteorological Reporter to the Government of India.

Madras.

- B. Central Museum.
A. Observatory.

Roorkee.

- p. Roorkee College.

Ireland.

Armagh.

- A. Observatory.

Belfast.

- AB. Queen's College.

Ireland (continued).

Cork.

- p. Philosophical Society.
AB. Queen's College.

Dublin.

- A. Observatory.
AB. National Library of Ireland.
B. Royal College of Surgeons in Ireland.
AB. Royal Dublin Society.
AB. Royal Irish Academy.

Galway.

- AB. Queen's College.

Italy.

Acireale.

- p. Accademia di Scienze, Lettere ed Arti.

Bologna.

- AB. Accademia delle Scienze dell' Istituto.

Catania.

- AB. Accademia Gioenia di Scienze Naturali.

Florence.

- p. Biblioteca Nazionale Centrale.
AB. Museo Botanico.
p. Reale Istituto di Studi Superiori.

Genoa.

- p. Società Ligustica di Scienze Naturali e Geografiche.

Milan.

- AB. Reale Istituto Lombardo di Scienze, Lettere ed Arti.
AB. Società Italiana di Scienze Naturali.

Modena.

- p. Le Stazioni Sperimentali Agrarie Italiane.

Naples.

- p. Società di Naturalisti.
AB. Società Reale, Accademia delle Scienze.
B. Stazione Zoologica (Dr. DOHN).

Padua.

- p. University.

Palermo.

- A. Circolo Matematico.
AB. Consiglio di Perfezionamento (Società di Scienze Naturali ed Economiche).
A. Reale Osservatorio.

Pisa.

- p. Il Nuovo Cimento.
p. Società Toscana di Scienze Naturali.

Rome.

- p. Accademia Pontificia de' Nuovi Lincei.
p. Rassegna delle Scienze Geologiche in Italia.
A. Reale Ufficio Centrale di Meteorologia e di Geodinamica, Collegio Romano.
AB. Reale Accademia dei Lincei.
p. R. Comitato Geologico d' Italia.
A. Specola Vaticana.

Italy (continued).

Rome (continued).

AB. Società Italiana delle Scienze.

Siena.

p. Reale Accademia dei Fisiocritici.

Turin.

p. Laboratorio di Fisiologia.

AB. Reale Accademia delle Scienze.

Venice.

p. Ateneo Veneto.

AB. Reale Istituto Veneto di Scienze, Lettere ed Arti.

Japan.

Tokiô.

AB. Imperial University.

p. Asiatic Society of Japan.

Java.

Buitenzorg.

p. Jardin Botanique.

Luxembourg.

Luxembourg.

p. Société des Sciences Naturelles.

Malta.

p. Public Library.

Mauritius.

p. Royal Society of Arts and Sciences.

Netherlands.

Amsterdam.

AB. Koninklijke Akademie van Wetenschappen.

p. K. Zoologisch Genootschap 'Natura Artis Magistra.'

Delft.

p. École Polytechnique.

Haarlem.

AB. Hollandsche Maatschappij der Wetenschappen.

p. Musée Teyler.

Leyden.

AB. University.

Rotterdam.

AB. Bataafsch Genootschap der Proefondervindelijke Wijsbegeerte.

Utrecht.

AB. Provinciaal Genootschap van Kunsten en Wetenschappen.

New Zealand.

Wellington.

AB. New Zealand Institute.

Norway.

Bergen.

AB. Bergenske Museum.

Christiania.

AB. Kongelige Norske Frederiks Universitet.

Norway (continued).

Tromsøe.

p. Museum.

Trondhjem.

AB. Kongelige Norske Videnskabers Selskab.

Portugal.

Coimbra.

AB. Universidade.

Lisbon.

AB. Academia Real das Sciencias.

p. Secção dos Trabalhos Geologicos de Portugal.

Oporto.

p. Annaes de Sciencias Naturaes.

Russia.

Dorpat.

AB. Université.

Irkutsk.

p. Société Impériale Russe de Géographie (Section de la Sibérie Orientale).

Kazan.

AB. Imperatorsky Kazansky Universitet.

p. Société Physico-Mathématique.

Kharkoff.

p. Section Médicale de la Société des Sciences Expérimentales, Université de Kharkow.

Kieff.

p. Société des Naturalistes.

Kronstadt.

p. Marine Observatory.

Moscow.

AB. Le Musée Public.

B. Société Impériale des Naturalistes.

Odessa.

p. Société des Naturalistes de la Nouvelle-Russie.

Pulkowa.

A. Nikolai Haupt-Sternwarte.

St. Petersburg.

AB. Académie Impériale des Sciences.

B. Archives des Sciences Biologiques.

AB. Comité Géologique.

AB. Ministry of Marine.

A. Observatoire Physique Central.

Scotland.

Aberdeen.

AB. University.

Edinburgh.

p. Geological Society.

p. Royal College of Physicians (Research Laboratory).

p. Royal Medical Society.

A. Royal Observatory.

p. Royal Physical Society.

p. Royal Scottish Society of Arts.

AB. Royal Society.

Scotland (continued).

Glasgow.

- AB. Mitchell Free Library.
- p. Natural History Society.
- p. Philosophical Society.

Servia.

Belgrade.

- p. Académie Royale de Serbie.

Sicily. (See ITALY.)

Spain.

Cadiz.

- A. Instituto y Observatorio de Marina de San Fernando.

Madrid.

- p. Comisión del Mapa Geológico de España.
- AB. Real Academia de Ciencias.

Sweden.

Gottenburg.

- AB. Kongl. Vetenskaps och Vitterhets Samhälle.

Lund.

- AB. Universitet.

Stockholm.

- A. Acta Mathematica.
- AB. Kongliga Svenska Vetenskaps-Akademie.
- AB. Sveriges Geologiska Undersökning

Upsala.

- AB. Universitet.

Switzerland.

Basel.

- p. Naturforschende Gesellschaft.

Bern.

- AB. Allg. Schweizerische Gesellschaft.
- p. Naturforschende Gesellschaft.

Geneva.

- AB. Société de Physique et d'Histoire Naturelle.
- AB. Institut National Genevois.

Lausanne.

- p. Société Vaudoise des Sciences Naturelles.

Neuchâtel.

- p. Société des Sciences Naturelles.

Zürich.

- AB. Das Schweizerische Polytechnikum.
- p. Naturforschende Gesellschaft.
- p. Sternwarte.

Tasmania.

Hobart.

- p. Royal Society of Tasmania.

United States.

Albany.

- AB. New York State Library.

United States (continued).

Annapolis.

- AB. Naval Academy.

Austin.

- p. Texas Academy of Sciences.

Baltimore.

- AB. Johns Hopkins University.

Berkeley.

- p. University of California.

Boston.

- AB. American Academy of Sciences.
- B. Boston Society of Natural History.
- A. Technological Institute.

Brooklyn.

- AB. Brooklyn Library.

Cambridge.

- AB. Harvard University.
- B. Museum of Comparative Zoology.

Chapel Hill (N.C.).

- p. Elisha Mitchell Scientific Society.

Charleston.

- p. Elliott Society of Science and Art of South Carolina.

Chicago.

- AB. Academy of Sciences.
- p. Astro-physical Journal.
- p. Field Columbian Museum.
- p. Journal of Comparative Neurology.

Davenport (Iowa).

- p. Academy of Natural Sciences.

Ithaca (N.Y.).

- A. Journal of Physical Chemistry.
- p. Physical Review (Cornell University).

Madison.

- p. Wisconsin Academy of Sciences.

Mount Hamilton (California).

- A. Lick Observatory.

New Haven (Conn.).

- AB. American Journal of Science.
- AB. Connecticut Academy of Arts and Sciences.

New York.

- p. American Geographical Society.
- A. American Mathematical Society.
- p. American Museum of Natural History.
- p. New York Academy of Sciences.
- p. New York Medical Journal.
- p. School of Mines, Columbia College.

Philadelphia.

- AB. Academy of Natural Sciences.
- AB. American Philosophical Society.
- p. Franklin Institute.
- p. Wagner Free Institute of Science

United States (continued).

Rochester (N.Y.).

p. Academy of Science.

St. Louis.

p. Academy of Science.

Salem (Mass.).

p. American Association for the Advancement of Science.

AB. Essex Institute.

San Francisco.

AB. California Academy of Sciences.

Washington.

AB. Patent Office.

United States (continued).

Washington (continued).

AB. Smithsonian Institution.

AB. United States Coast Survey.

B. United States Commission of Fish and Fisheries.

AB. United States Geological Survey.

AB. United States Naval Observatory.

p. United States Department of Agriculture.

A. United States Department of Agriculture (Weather Bureau).

West Point (N.Y.)

AB. United States Military Academy.

ADJUDICATION of the MEDALS of the ROYAL SOCIETY for the year 1899,
by the PRESIDENT and COUNCIL.

The COPLEY MEDAL to the Right Hon. Lord RAYLEIGH, F.R.S., in recognition of his contributions to Physical Science.

A ROYAL MEDAL to Professor G. F. FITZGERALD, F.R.S., for his contributions to Physical Science, especially in the domains of Optics and Electricity.

A ROYAL MEDAL to Professor W. C. MCINTOSH, F.R.S., for his important monographs on British Marine Zoology and on the Fishery Industries.

The DAVY MEDAL to Dr. EDWARD SCHUNCK, F.R.S., for his researches on Madder, Indigo, and Chlorophyll.

The Bakerian Lecture for 1899, "The Crystalline Structure of Metals," was delivered by Professor J. A. EWING, F.R.S., and Mr. W. ROSENHAIN, on May 18, 1899.

The Croonian Lecture for 1899, "On the Relation of Motion in Animals and Plants to the Electrical Phenomena which are associated with it," was delivered by Professor BURDON SANDERSON, F.R.S., on March 16, 1899.



PHILOSOPHICAL TRANSACTIONS.

I. *On the Recovery of Iron from Overstrain.*

By JAMES MUIR, B.Sc., *Trinity College, Cambridge* (1851 *Exhibition Science Research Scholar, Glasgow University*).

Communicated by Professor EWING, F.R.S.

Received January 25,—Read February 9, 1899.

It has long been known that iron which has been overstrained in tension—that is to say strained beyond the yield-point so that it suffers a permanent stretch—possesses very different elastic properties from the same iron in its primitive condition. The material is said to be “hardened” by stretching,* since the ultimate effect of such treatment is to raise the elastic limit and reduce the ductility of the material.

More recently, attention has been called to the fact that, primarily, the result of tensile overstrain is to make iron assume a semi-plastic state, so that the elastic limit, instead of being raised by stretching, is first of all lowered, it may be to zero.† This plasticity may be shown by applying a comparatively small load to a bar of iron or steel which has just been overstrained by the application and removal of a large stretching load. When the small load is put on, the bar will be found to elongate further than it would had the material been in its primitive state; and a slight continued elongation—a “creeping”—may occur after the small load has been applied. If this load be withdrawn, a quite appreciable permanent, or semi-permanent, set will be found to have been produced; a set which diminishes slightly,

* EWING, “On Certain Effects of Stress,” ‘Proc. Roy. Soc.’ No. 205, 1880. The raising of the elastic limit due to stretching seems to have been first noted in 1865 by THALÉN. See a translation of his paper in the ‘Phil. Mag.’ for September of that year.

† BAUSCHINGER, “Ueber die Veränderung der Elasticitätsgrenze,” ‘Civilingénieur,’ 1881, or “Mittheilungen aus dem mechanisch-technischen Laboratorium der K. Polytechnischen Schule in München.” An account of BAUSCHINGER’S work is given in UNWIN’S book on “Testing of Materials of Construction.”

EWING, “On Measurements of Small Strains in the Testing of Materials and Structures,” ‘Proc. Roy. Soc.’ vol. 58, April, 1895.

and, if small, may vanish, provided time be allowed for backward creeping to take effect. It may also be shown that, if the re-applied load be increased, the elongation produced will increase in a greater proportion. Thus, if a stress-strain curve be obtained from a recently overstrained bar of iron or steel, it will show, even for small loads, a marked falling away from the straight line which would indicate obedience to Hooke's law.

It is the recovery from this semi-plastic state induced by overstrain to a condition of perfect or nearly perfect elasticity with raised elastic limit, that is referred to in the title of this paper. Such recovery is known to be effected by mere lapse of time,* and the object of the experiments about to be described is to show the effect of moderate temperature, of mechanical vibration, and of magnetic agitation, on this slow return to the elastic state, and further to illustrate this recovery by means of compression tests. One section of the paper deals with the phenomenon of hysteresis in the relation of extension to stress, which is exhibited in a marked degree by iron in the overstrained state. Incidentally, attention will be called to subsidiary points of interest.

The experiments were carried out in the Engineering Laboratory of Cambridge University, and were the outcome of suggestions by Professor EWING. It was on his suggestion that the effect of moderate temperature on recovery from overstrain was tried, and the result of that trial led to much of the work incorporated in this paper.

Before going into details of the experiments it may be of interest to give, drawn to a small scale, an ordinary complete stress-strain diagram, such as is obtained in the testing of iron or steel. The period in the history of iron subjected to tensile stress which is about to be investigated, may thus be more clearly indicated. The curve given in Diagram No. I. was sketched by hand, roughly, from data obtained from the experiments which will be described later. It applies to steel not previously submitted to overstrain.

For the portion *ab* of this curve Hooke's law is obeyed. At *b* the yield-point occurs, and as soon as this point is passed the material becomes overstrained. During the large yielding which takes place at the yield-point the load may be reduced without causing the extension to stop. After stretching by a large amount as compared with elastic extension, the material will be found to have hardened; so that to produce further yielding the load must be increased. The stress-strain diagram may now be represented by some such curve as *cd*. If at *d* the load be removed, and at once gradually replaced, then the stress-strain curve may follow a path such as *de*, *ef*. These curves *de* and *ef*, when obtained in such a manner that the exten-

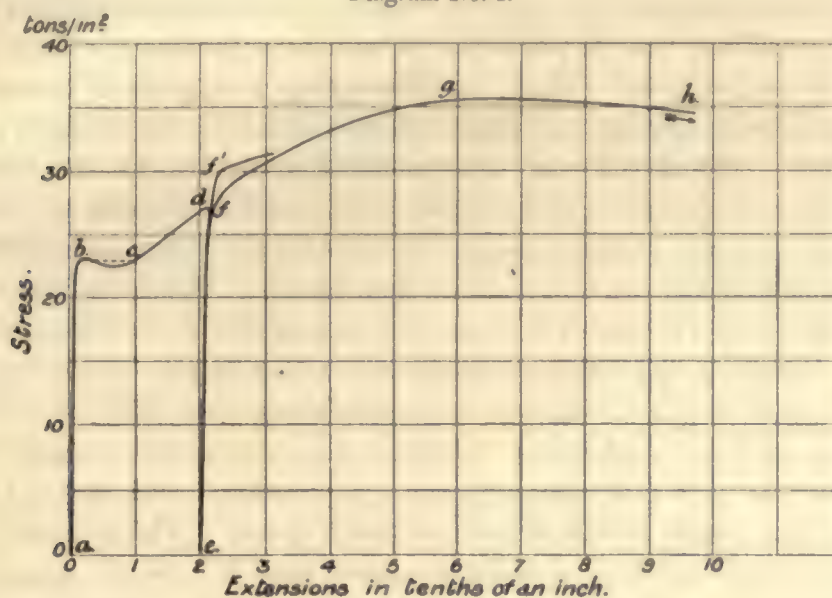
* BAUSCHINGER, 'DINGLER'S Journal,' vol. 224, p. 5, and papers already cited.

EWING, both papers cited above.

Reference might also be made to Lord KELVIN'S discovery of the effect of a Sunday's rest on wires which had been subjected to torsional vibrations throughout the preceding week.—See article, "Elasticity," 'Encycl. Brit.'

sions can be plotted to a much larger scale, show the imperfect elasticity of recently overstrained iron which has been referred to above; that is, they show that the material is semi-plastic. If time be allowed to elapse between unloading and reloading, the recovery from the effect of overstrain may be shown in a diagram like the present, by some such curve as ef'' . When no interval of time is allowed to elapse between the removal and the replacement of the load, then the stress-strain curve is continued in the manner shown by fg , until a point g is reached, at which local

Diagram No. I.



extension sets in. When this happens the stress may be diminished, and fracture may take place at a load lower than that at which local extension occurred. The stress per square inch of fractured area is, however, found to be much greater than the stress per square inch of the actual area when local elongation began.

The Apparatus and the Material.

The straining and testing in the following experiments was done by means of the 50-ton Wicksteed single-lever hydraulic testing machine of the Cambridge Engineering Laboratory. With this machine the magnitude of the load applied could be read in tons to a second decimal place by means of a vernier, and to a third decimal place roughly by estimation. Thus a load could be applied accurately if necessary to, it may be said, $\frac{1}{1000}$ th of a ton.

The small strains of extension were measured by Professor EWING's extensometer.*

* For a full description of this instrument see the paper already cited "On the Measurement of Small Strains, &c.," 'Proc. Roy. Soc.,' vol. 58, April, 1895.

This instrument gave the extension occurring in the middle 8 inches of the length of the specimen under test. It enabled elongations to be measured to $\frac{1}{50000}$ th of an inch, and to be measured to that degree of precision with ease and confidence. The instrument was found especially convenient on account of the facility with which it could (by the aid of a distance-piece) be immediately re-applied to a specimen which had just been strained beyond its yield-point; and also on account of the readiness with which the correct adjustment of the instrument itself could be tested.

The specimens employed were, with one or two exceptions, 18 to 20-inch lengths of steel-rod, 1 inch in diameter, of a quality which may be described as semi-mild. The details of the particular rods employed in the various experiments will be given when these come to be described. Here, as illustrating the general character of the material, the chemical analyses and elastic characteristics of two of the bars made use of will be given. The first is that from which diagram No. IX. has been obtained. A specimen from it showed a well-defined yield-point at a stress of 23 tons to the square inch, and gave an ultimate strength of $36\frac{1}{2}$ tons per square inch of original area, with an elongation of $22\frac{1}{2}$ per cent. on an 8-inch length. The second bar is that from which diagrams Nos. IV. and VII. have been obtained; it was characterised by a small flaw running up the centre through the whole length of the bar. A well-defined yield-point was not obtained with specimens from this bar; there was a distinct departure from obedience to HOOKE'S law, at a stress of about 22 tons per square inch, but the yield-point should, perhaps, be placed as much as 6 or 7 tons higher than this stress, at which elastic behaviour broke down.* The ultimate strength of the material as obtained from a short specimen was 39 tons per square inch, the elongation being only about $20\frac{1}{2}$ per cent. on a 3-inch length. The chemical analyses of these two bars were kindly supplied by Messrs. EDGAR ALLEN and Co., Sheffield, from whom the material was obtained; they are as follows:—

	Bar of diagram No. IX.	Bar of diagrams Nos. IV. and VII.
Carbon	0.430	0.450
Silicon	0.112	0.093
Sulphur	0.010	0.012
Phosphorus	0.016	0.021
Manganese	0.450	0.410
Iron (by difference)	98.982	99.014
	100.000	100.000

* See the first column of the table on p. 15.

The Method of Experimenting.

The general procedure adopted in experimenting will now be described. First, the diameter of the specimen was determined from the mean of ten micrometer readings, taken at five equidistant places along the 8-inch length to which the extensometer was to be applied. For example, the following readings were obtained for a certain unturned specimen :—

$$\text{Diameter} = \left\{ \begin{array}{ccccc} 1''\cdot0069 & 71 & 65 & 64 & 61 \\ & 70 & 71 & 71 & 59 & 54 \end{array} \right\} = 1''\cdot0066.$$

Not only was this done for virgin specimens, but whenever a yield-point had been passed, the diameter was re-determined by means of fresh readings. For example, the specimen already instanced was subjected to a pull gradually increasing to 35 tons to the square inch of original section, the yield-point occurring at 23 tons per square inch. After the removal of this large stretching load the new diameter was determined from the following readings :—

$$\text{Diameter} = \left\{ \begin{array}{ccccc} 0''\cdot9918 & 21 & 18 & 20 & 25 \\ & 14 & 22 & 24 & 15 & 24 \end{array} \right\} = 0\cdot9920 \text{ of an inch.}$$

After the determination of the diameter of a specimen at each stage of an experiment, a table was formulated, from which the total load applied could be translated into tons per square inch of section, the stress being in every case measured with reference to the section at the beginning of each separate test.

These preliminaries having been completed, the specimen was put into the testing machine, the extensometer was attached, and the load was gradually applied. Extensometer readings were taken sometimes only after the addition of every four tons of stress, sometimes after each ton, sometimes after each half or quarter ton, according to judgment.

The following two series of readings are given for a typical experiment ; they will serve to explain the usual procedure. The first series shows the elastic properties of a certain virgin specimen ; the second shows the plastic nature of the same specimen immediately after the overstrain produced by the primary loading.

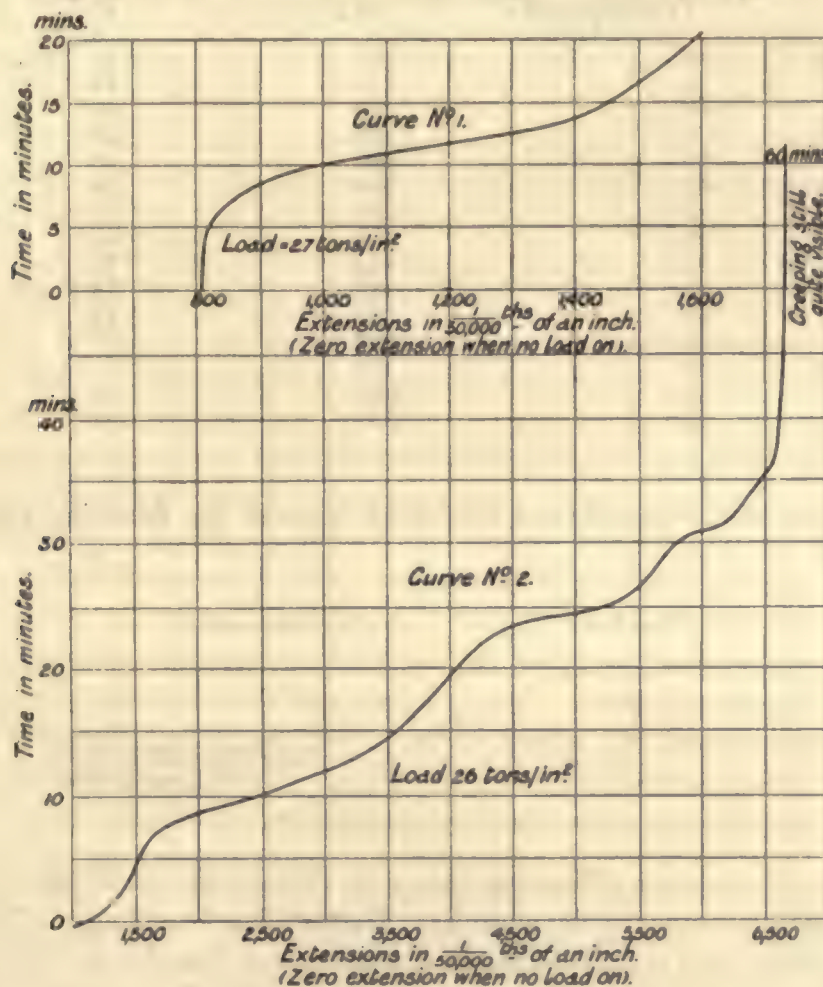
Stress in tons per square inch.	Total load in tons.	Extensometer readings. Unit = $\frac{1}{50000}$ of an inch.	Differences.
0	0	0	
1	0.79	30	30
2	1.58	60	30
4	3.16	120	60
6	&c.	180	60
8	...	240	60
10	...	300	60
12	...	360	60
14	...	421	61
16	...	481	60
18	...	540	59
20	...	600	60
22	...	660	60
24	...	720	60
25	...	750	30
26	...	780	30
27	...	810	30
		still 810 after 4 minutes,	
		but 830 " 6 "	
		&c. &c. (see Curve No. 1, Diagram II.)	
		1595 after 20 minutes	
27½	...	1700 and then quickly out of range	
30 put on gradually and kept on for 3 minutes, the beam of the testing machine remaining steady			

These figures show that this specimen has accurately obeyed HOOKE'S law, until a stress of 27 tons per square inch was attained. At this load the yield-point was expected to occur, and although the extensometer reading obtained gave no evidence of the proximity of such a point, by simply allowing the load to remain on for a short time (4 minutes) the creeping recorded above set in, or perhaps spread from without to within the 8-inch length under test.* The yield-point, with this specimen, has, therefore, coincided with the elastic limit as accurately as the extensometer can measure. Usually, in testing, imperfection of elasticity is shown before the yield-point is reached, and if a load less than that at the yield-point be allowed to act for some time, then a slight creeping probably supervenes. When, however, a bar, like that referred to above, has shown very perfect elasticity up to the yield-point, it is probable that a load very little under that at which the yield-point occurs could be sustained for an indefinite time without creeping taking place. Even although slight imperfection of elasticity be shown before the yield-point, experiments showed that no creeping need necessarily occur for a pause in the loading of at least a night's duration.

* The fact that yielding takes some time to start has already been recorded by Professor EWING in his paper cited above, "On Measurements of Small Strains, &c." (see pp. 135 and 136). He has noticed that yielding may begin in a part of the bar lying outside the 8-inch length to which the extensometer is applied, and may gradually spread along the bar.

The manner in which yielding under a constant load proceeds after the yield-point has just been passed is often very irregular. The curves given on Diagram II. illustrate this yielding with time for two entirely different specimens. The first shows the creeping referred to above as having started 4 minutes after the application of the load which was its cause. The second curve shows a larger yielding of much longer duration. It occurred under a load of 26 tons per square inch, but before this load

Diagram No. II.—(Manner in which yielding occurs at the yield-point.)



was attained—when 25 and $25\frac{1}{2}$ tons per square inch were acting—considerable creeping had already taken place. The readings from which these curves have been obtained were taken at intervals of one minute.

To return to the table of figures given above, the maximum load (of 30 tons to the square inch of original section) was found, after its removal, to have produced a permanent set of 0.22 of an inch on the 8-inch length; this corresponds to an extensometer reading of 11,000; such a reading is, of course, far beyond the range of the extensometer. Immediately after the maximum load had been removed, the

diameter of the specimen was re-measured and the reduced section determined. The extensometer was then re-applied, the specimen was re-loaded, and the following readings observed :—

Tons per sq. in. (of reduced section).	Extensometer readings.	Differences.
0	0	
1 (= 0.77 ton of total load)	30	30
2	61	31
4	125	64
6	190	65
8	260	70
10	329	69
12	399	70
14	469	70
16	539	70
18	613	74
20	687	74
22	764	77
24	845	81
26	930	85
28	1028	98
30	1150	122

The load was now removed, and during its removal the following three readings were taken :

Tons/inch ² .	Extensometer.
20	830
10	477
0	60 but diminishing slightly with lapse of time

The series of increasing differences shown in this second table plainly indicates a change in the elastic state of the material. HOOKE'S law is no longer obeyed.

This augmentation of the differences is, to some extent, associated with creeping, and to a greater extent, the higher is the applied load. Thus it is essential, if consistent results are to be obtained, that the interval of time which elapses between successive readings should always be kept the same. If a pause had been allowed to occur after the addition of any of the higher loads in this second table, then, owing to prolonged creeping, a larger difference would have been obtained than is recorded above. On proceeding with the loading, however, the immediately succeeding difference, or differences, would have been smaller than according to the table. For had there been no interruption, part of the creeping which occurred during the pause would have been recorded on the addition of the subsequent loads.

In experiments on a virgin piece of which the first table given above is typical, the time element does not enter, for there is no perceptible creeping until the yield-point is all but reached.

Slow Recovery of Elasticity with lapse of Time.

Before proceeding to describe the effect of special treatments on recovery from tensile overstrain, I give two instances of the slow recovery from overstrain with lapse of time, similar to the examples already given by Professor EWING.*

The curves in Diagram No. IIIA. illustrate this slow recovery for a specimen of 1 inch round steel rod, which has been strained to or very little beyond its yield-point. The material had an ultimate strength of 37 tons per square inch of original area, the total elongation being almost 23 per cent. on an 8-inch length. The yield-point was well defined and occurred at a stress slightly under 27 tons to the square inch. The readings from which the various curves have been plotted are given in the table on p. 11. The curves were obtained in the usual manner, the stresses being plotted as ordinates, and the corresponding extensions as abscissæ.

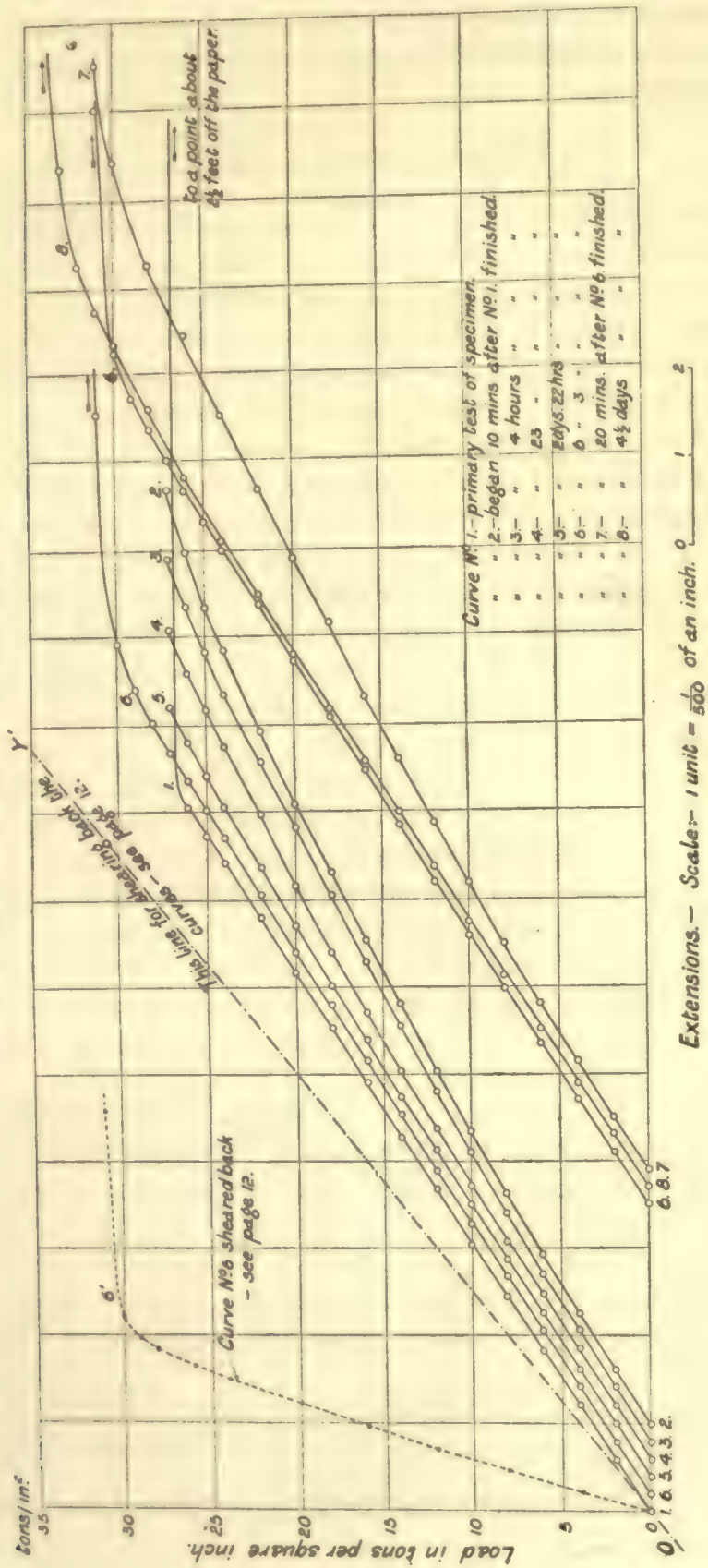
Curve No. 1 of Diagram IIIA. is a record of the primary test of the specimen. It shows that HOOKE's law has been obeyed up to a load of 26 tons to the square inch; and that before 27 tons there was a well-marked yield-point. This load of 27 tons per square inch was kept on for two minutes, by which time rapid stretching had ceased, as was shown by the beam of the testing machine remaining stationary. There was still a slow creeping, which probably would have continued for hours or days, becoming however slower and slower. Curve No. 2 represents a test performed as shortly after the removal of this load as the remeasurement of the diameter and the calculation of the reduced area would permit: it illustrates the semi-plastic condition of the material immediately after overstrain. In the plotting of this, and all subsequent curves in the diagram, it will be noticed that the origin for the measurement of extensions has been displaced; this was merely to keep the curves distinct and to facilitate comparison.

Curves Nos. 3, 4, 5, and 6, obtained at succeeding intervals, illustrate the gradual recovery of the elasticity lost by the overstrain. This recovery will be noticed to be quickest at first, and latterly to be very slow. In Curves 3, 4, and 5 the load was not allowed to exceed 27 tons per square inch. Curve No. 6 shows the recovery to have been nearly, though not quite, perfect after the material had been allowed to rest for 6 days 3 hours. In this test the load was gradually increased beyond the 27 tons, and a new yield-point was not obtained till rather over 30 tons to the square inch was reached.

Curve No. 7 shows the plastic nature of the material immediately after this second overstrain, and No. 8 the condition after 4 days' rest. Thus after 4 days the recovery

* See page 139, &c., of his paper "On Measurements of Small Strains, &c."

Diagram No. IIIA.—(Slow recovery with lapse of time.)



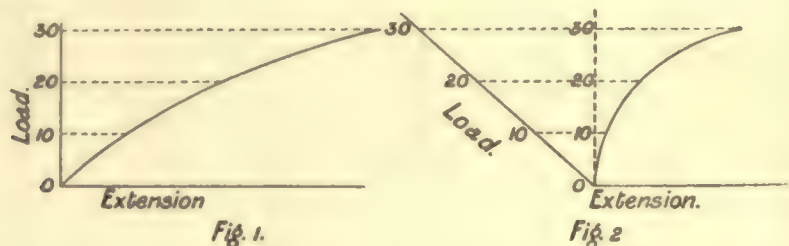
was by no means perfect, and on increasing the load beyond the 30 tons an almost immediate falling away was observed, and (as is shown in the curve) a third, rather indefinite, yield-point was indicated. Further yield-points might have been obtained had this treatment been proceeded with.

TABLE giving readings for Diagram No. III. (Slow recovery with time).

Load in tons/in ² .	Extensometer readings for various curves of Diagram III.							
	No. 1. Zero time.	No. 2. 10 mins.	No. 3. 4 hours.	No. 4. 23 hours.	No. 5. 2 days 22 hours.	No. 6. 6 days 3 hours.	No. 7. 20 mins. (No. 6, zero.)	No. 8. 4 days (No. 6, zero.)
0	0	0	0	0	0	0	0	0
2	60	62	62	61	61	60	61	60
4	121	125	128	125	122	122	127	120
6	182	192	191	188	186	186	191	181
8	243	262	260	249	248	249	260	243
10	304	333	330	311	310	309	330	305
12	368	405	401	378	372	370	397	368
14	428	481	477	444	434	433	471	429
16	491	553	550	511	500	498	542	489
18	553	631	625	581	562	560	626	549
20	618	709	701	658	630	621	700	610
22	680	793	779	738	698	687	778	678
24	742	883	855	817	765	750	860	740
25	772	933	902	859	801	781		
26	803	999	953	900	841	816	942	810
27	Out of range	1068 to 1117 in 3 mins. }	1010 to 1035 in 3 mins. }	949 to 978 in 3 mins. }	881 to 897 in 3 mins. }	850		
28	884	1035	889
29	921		
30	972	1152	964
31	1251 and then very large yielding	1262 to 1382 in 2 mins. }	1004
32	1055
33	1166
34	Very large yielding
Load removed. 0	...	128 to 113 in 4 mins. }	51 to 39 in 4 mins. }	36 to 29 in 15 mins. }	23 to 17	...	241 to 228	

The "Shearing Back" of the Curves.

It will have been noticed that, owing to the extensions being plotted to an unusually large scale, the curves occupy an inconvenient amount of space. This may be avoided by adopting a geometric artifice, suggested by Professor EWING, of "shearing back" the curves; that is, retaining the same scale of measurement, an amount is deducted from each extension proportional to the load producing it. For example, if extensions of 120, 240, 360 were produced by loads of 4, 8, and 12 tons per square inch respectively, the extensions might be diminished by, say, 100 units per 4 tons of load, and plotted as 20, 40, and 60. Another way of expressing this is to say that in the diagram the axis from which extensions are measured may simply be considered as tilted back in the manner shown below by fig. 2. Fig. 1 shows a curve drawn with ordinary rectangular axes, and fig. 2 the same curve "sheared back."



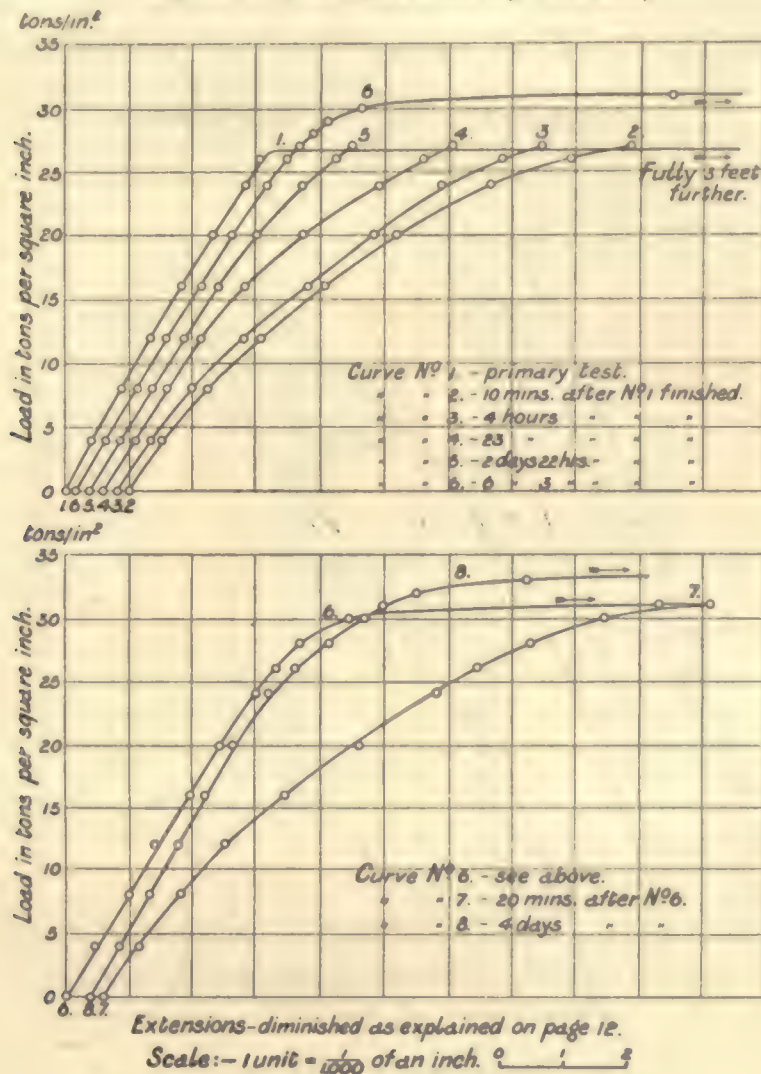
Referring again to Diagram No. IIIA., the process of "shearing back" is performed graphically on the single Curve No. 6 by adopting an oblique base line, OY', the distance from which of each point of the curve is measured horizontally and re-plotted from the vertical base line, Curve No. 6' being obtained. Besides the convenience of space gained, this foreshortening of the curves by diminishing the rates of extension renders a more obvious comparison of similar, but slightly different, curves, and emphasises any irregularities there may be in the extensometer readings. It should thus be remembered that in a stress-strain curve which has been "sheared back" inequalities in extension are exaggerated, since the relations they bear to the total extensions are not shown.

In Diagram No. IIIB. all the curves of Diagram No. IIIA.* are shown sheared back by the method just explained, and in all similar diagrams to be shown in this paper the curves will be subjected to the same treatment. In all cases the amount of shearing of the curves is the same—the extensions are always diminished by $\frac{100}{50000}$ ths of an inch for every 4 tons of stress. The scale for the measurement of extensions

* Since Diagram IIIA. has been reproduced one-half full size, while Diagram IIIB. (and all other diagrams in the paper) have been reproduced to a two-thirds scale, the two Diagrams IIIA. and IIIB. are not absolutely comparable. Besides this difference due to reproduction, the scale for the measurement of load in IIIB. was originally only half that in IIIA.

will be kept the same for all analogous diagrams, but that for the measurement of load will be varied, in order to get the different diagrams suitably spaced.

Diagram No. IIIb. — (Slow recovery with time.)



Second Example of Slow Recovery with Lapse of Time.

In Diagram No. IV. there is shown the slow recovery from overstrain of a slightly different quality of steel under somewhat different conditions from those of the last example, while in the accompanying table the figures are given from which the various curves of that diagram have been plotted. The material is that described second on p. 4.

An examination of the differences given in the first column of the table on p. 15 will show that, although during the primary loading of the specimen, considerable yielding set in at a stress of 22 tons per square inch, it was not until almost 29 tons that such

Curve No. 2 illustrates the semi-plastic condition of the material immediately after the removal of the overstraining load; while Curves Nos. 3, 4, and 5 show the progress made towards recovery, 2, 7, and 17 days respectively, after the material had

TABLE of Readings for Diagram IV. (Slow recovery with time.)

Load in tons/in ² .	Extensometer readings for the various curves.				
	No. 1. Zero time.	No. 2. 15 mins.	No. 3. 2 days.	No. 4. 7 days.	No. 5. 17 days.
0	0	0	0	0	0
2	60	62	61	61	60
4	121	129	122	122	120
6	181	190	188	182	179
8	241	259	247	242	239
10	301	329	309	302	299
12	361	398	370	363	359
14	422	468	433	424	419
16	482	539	499	485	479
18	543	609	568	545	539
20	604	681	637	612	600
21	634	719	669	643	630
22	684	755	706	674	661
23	750	791	740	705	692
24	810	830	779	737	725
25	889	869	815	770	757
26	998	909	851	802	788
27	1140	949	890	834	819
28	1440	991	930	865	850
29	— Out of	1035	970	903	882
30	range, say 6500	1079	1011	934	915
31	...	1124	1058	967	948
32	...	1171	1104	1002	979
33	Load slowly in- creased to 35 tons, and then removed.	1225	1149	1036	1012
34		1279	1199	1074	1048
35		1349	1250	1133	1079
1 minute }		1368	1262		
30	...	1207	1108	980	tons/in ² . 35½ 1096
25	...	1037	940	820	36 1111
20	...	863	772	666	36½ 1129
15	...	689	601	510	37 1146
10	...	501	425	352	Extensometer re- moved.
5	...	305	237	187	Break in grips at 41 tons/in ² .
0	0.31 of an inch.	85	39	15	
Time	...	6 mins. 78 } 2 days 63 }	6 mins. 30 }		

been overstrained. The manner in which contraction takes place during the removal of the load is shown by dotted lines in Curves Nos. 2, 3, and 4, and it will be noticed that comparatively great retraction takes place as the lowest loads are removed. The test illustrated by Curve No. 5 shows that after 17 days' rest recovery was practically

perfect, the material approximately obeying Hooke's law up to the maximum stress of 35 tons per square inch. The load in this test was therefore increased beyond its previous maximum amount. The extensometer, however, was shortly removed for fear of a sudden break, so that the top part of Curve No. 5 (shown dotted in the diagram) was not obtained from extensometer readings. At a stress of about 41 tons per square inch the specimen suddenly broke, unfortunately in the machine grips; before this stress was reached no yield-point had been passed, or it would have been detected by a rapid falling of the horizontal beam of the testing machine.

Recovery under Stress, and Effects of Hysteresis.

Experiments were carried out to test the effect of keeping an overstrained specimen loaded, instead of allowing it to rest in an unstressed condition, and it was found that the material, whether kept stressed or unstressed, recovered at practically the same rate.

In the following table extensometer readings are given, which show the gradual recovery from overstrain of two specimens, A and B. A was kept loaded to the maximum stress employed to produce overstrain, while B was allowed to rest free from load.

TABLE comparing Recovery under Stress and Recovery when no Load was Acting.

Load in lbs./in ² .	Extensometer readings.					
	Immediately after over-strain.		10 days after.		40 days after.	
	A.	B.	A.	B.	A.	B.
500	0	0	0	0	0	0
10,000	137	135	121	129	129	129
20,000	286	287	269	270	265	269
30,000	446	448	426	427	410	410
40,000	610	612	587	589	560	561
50,000	795	805	759	760	717	719
55,000	901	925	842	859	795	799

This experiment was carried out during a vacation in the Engineering Laboratory of Glasgow University (Professor BARR having kindly granted the use of apparatus and laboratory), so that the conditions of experiment are somewhat different from those explained at the beginning of this paper. A 10-ton single-lever testing machine was employed, and the load applied by thousands of pounds, instead of by tons. Professor EWING's extensometer was still used. The material tested was a half-inch

rod of fairly mild steel. It gave an ultimate strength of about 32 tons per square inch, with an elongation of $26\frac{1}{2}$ per cent. on an 8-inch length. The primary yield-point occurred at a stress of 48,000 lbs., or about $21\frac{1}{2}$ tons per square inch. It will be noticed from the table of figures that this material recovered very slowly, for even after forty days' rest recovery was by no means complete. Specimen A of the above table was further tested after about three and a-half months, and considerable imperfection of elasticity still found.

Although the table given above shows close agreement between the elastic states of the material in the two cases, there was really an interesting difference between them. This is clearly shown by Diagram No. V. Curves A and B in that diagram illustrate

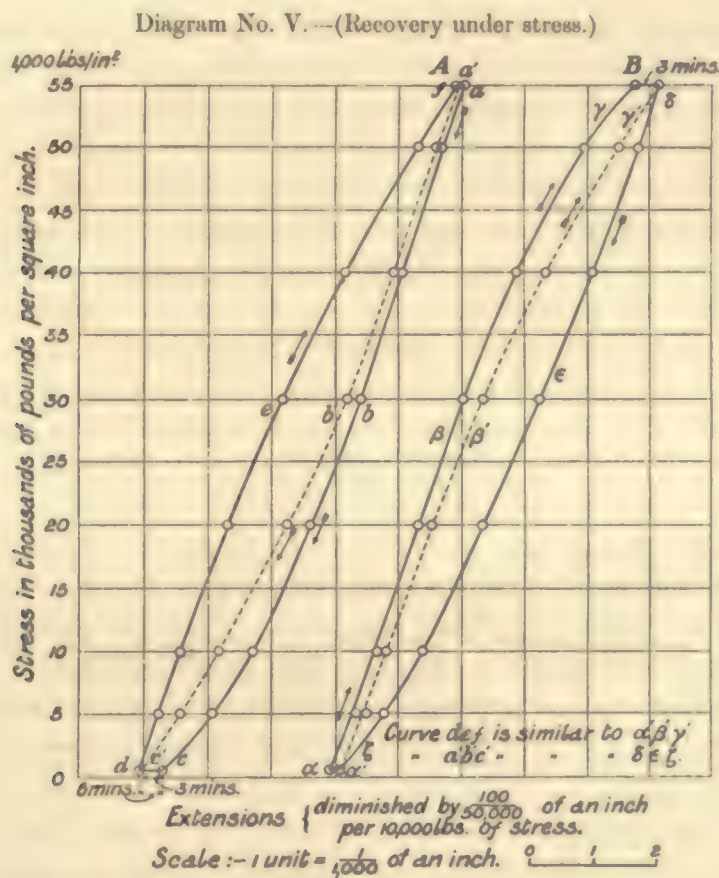


Fig. A represents the elastic condition of an overstrained specimen, which had been resting for forty days at a stress of 55,000 lbs./in².

Fig. B represents the elastic condition of an overstrained specimen, which had been resting for forty days free from stress.

the testing of the two specimens after the forty days' rest referred to above; the last thirty of these days were uninterrupted by any intermediate testing, and during that time A was in the testing machine, with a load of 55,000 lbs. per square inch applied to it. The extensometer having been applied to A, the load was gradually removed,

and readings taken, from which the part of Curve A lettered *abc* was plotted. This shows that, while a considerable proportion of the load was being removed, contraction occurred quite elastically, a straight line being first obtained at an inclination giving the Young's modulus for the material. Latterly, however, as more load was withdrawn, the retraction became more rapid, and after all load had been removed, creeping was observed to continue in a marked fashion for a few minutes, as is shown by the horizontal line *cd*. The load was now increased, and the curve *def* obtained. At the maximum stress slight creeping occurred, and then the load was once more removed, and curve *a'b'c'* was plotted from the extensometer readings taken. This curve differs distinctly from *abc* (obtained on first removing the load), the material behaving less elastically during the early part of this second removal of the load. The curve *defa'b'c'*, however, represents an approximately cyclic state, which illustrates the imperfectly elastic condition of the material of specimen A at the time in question. When such a cycle—due to hysteresis in the relation of extension to load—is performed, work is done on the specimen, and the energy so spent is no doubt dissipated as heat.

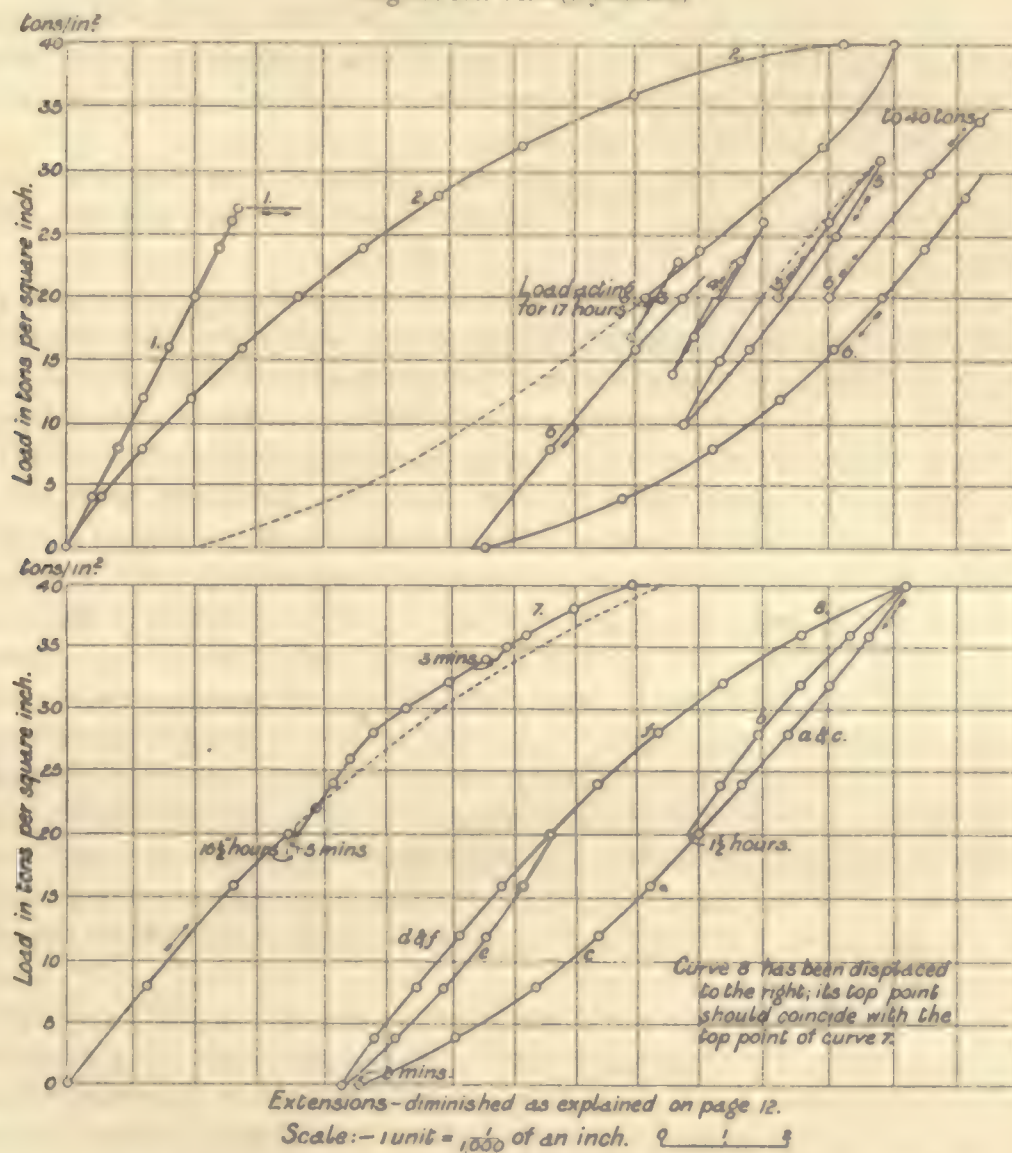
Specimen B, which had been resting for forty days free from load, was next put into the testing machine, and the load was gradually applied. The result of the first loading is shown by the part of fig. B, Diagram V., lettered $\alpha\beta\gamma$. This curve is straight for a considerable portion ($\alpha\beta$)—the material at first approximately obeying the elastic law—but latterly greater extension occurred, and at the highest load creeping continued very obviously for a short time. The load was then removed, and curve $\delta\epsilon\zeta$ obtained. This curve resembles closely the part *a'b'c'* of Curve A, not the part *abc*. Specimen B was next reloaded, and curve $\alpha'\beta'\gamma'$ illustrates the manner of yielding. This curve differs from $\alpha\beta\gamma$ just as *a'b'c'* differed from *abc*. A cyclic state has now been attained, and the cycle $\alpha'\beta'\gamma'\delta\epsilon\zeta$ closely resembles that got with specimen A, which had been allowed to rest under high stress. The readings for curves *def* and $\alpha'\beta'\gamma'$ of these cycles were compared in the table given above.

It will have been noticed that it is not only the cycles ultimately obtained which are analogous in the two figures of Diagram V., but that, if one of the figures, say A, be turned upside down, then the three curves of that figure closely resemble the three curves of the other figure, B. Considering in particular the curves first obtained in the two cases, viz., *abc* and $\alpha\beta\gamma$, it will be seen that they consist of two parts. There is first a range of almost perfect elasticity, then an elastic limit is passed, and greater extension or retraction obtained, according to the curve in question. The breaking up in the structure of the material, which occurs after this elastic limit has been passed (by a decreasing or an increasing load, as the case may be), is probably analogous to the much greater breaking up which occurs on the passage of a yield-point.

In Diagram No. VI., there is illustrated the effect, on an overstrained specimen, of keeping an intermediate load acting for some time; and it will be seen that the process of recovery tends to produce an elastic range about the position of continued

stress. The experiments illustrated by this diagram were carried out in the Cambridge Engineering Laboratory, hence the loading is performed in tons (not in pounds) per square inch. The material used is very similar to that employed to obtain Diagram No. III., so that the rate of recovery from overstrain is much quicker than with the material of Diagram V.

Diagram No. VI. (Hysteresis).



Curves 4, 5 and 6 are displaced to the right—they should be continuous with one another and with Curves 2 and 3.

Curve No. 1 of Diagram VI. shows the primary elastic properties of the steel rod considered. After this first test, the specimen was largely overstrained and allowed to recover. On testing, it was then found to give a yield-point at about 40 tons per

square inch, and immediately after this yield-point had been passed, Curve No. 2 was obtained.

It will be noticed from the diagram that in Curve No. 2, the removal of the load was stopped midway and the stress of 20 tons per square inch allowed to act over a night. Had the load been entirely removed, then Curve No. 2 would have continued in some such fashion as is illustrated by the dotted line in the diagram.

The continued action of the load of 20 tons was found in the morning to have produced the slight extension shown. On then testing the specimen by first increasing and then decreasing the load for a short range on either side, Curve No. 3 was first obtained, and then Curves Nos. 4, 5 and 6.

Curve No. 3 shows a short range of nearly, though not quite, perfect elasticity. A slight discrepancy of $\frac{1}{50000}$ th of an inch was obtained on each side of the starting position.

Curves Nos. 4, 5 and 6 show how elastic behaviour is departed from, and greater and greater indications of hysteresis obtained as the range of loading is increased.

Curve No. 7, drawn on the bottom half of Diagram VI., shows the effect of applying a load of 20 tons to this same specimen, and allowing it to act for over sixteen hours before proceeding with the loading. That is, the effect produced by a prolonged pause in the loading of an overstrained specimen is shown. After the pause, the curve starts off at a much steeper gradient; but shortly it falls back again to a rather less inclination than if there had been no interruption in the loading. The dotted line in Curve 7 shows the manner in which the curve would have continued had no pause occurred in the loading. This continuation was accurately known; for previously the specimen had been loaded to 40 tons, three times in succession, and the last two applications had given very accurately the same curve—no two readings differing by more than $\frac{2}{50000}$ ths of an inch. At the stress of 34 tons, in Curve No. 7, the effect of a three minutes' pause is shown to be similar to, but of course much smaller than, the effect of the long pause at 20 tons. This slight effect at the higher load may, however, be explained by simply considering that if creeping be allowed to occur at any load, then a small increase of load cannot be expected to produce so great an extension as it otherwise would.

After Curve No. 7 was obtained, the complete cycle represented by Curve No. 8 was gone through. The part of this cycle lettered *a* represents the partial removal of the load from Curve No. 7. The stress was only reduced to 20 tons, and then one and a-half hours were allowed to elapse. Slight back-creeping occurred instead of forward-creeping, such as happened in Curve No. 2. The load was then increased and Curve *b* obtained. This curve arrived very accurately at the same top point as Curve *a*. The load was then entirely removed, and Curve *c*, which coincides so far with Curve *a*, was obtained. After a pause of five minutes under no load, during which back-creeping showed itself, the load was re-applied to 20 tons (Curve *d*), decreased to zero (Curve *e*), and then increased to 40 tons (Curve *f*),

which completed the large cycle of loading. The hysteresis exhibited by a cycle such as this may be represented numerically by expressing the breadth of the cycle at any stress, as a fraction of the total elongation of the specimen. If this be done, the hysteresis, in the relation of strain to stress, which recently overstrained iron has just been shown to exhibit, may be compared with that observed with ordinary material by Professor EWING in experiments on very long wires.* In Professor EWING's experiments, the wires were subjected many times to a certain range of stress, and the extension at half the range was observed both as the load was applied and as it was removed. The latter extension was found, due to hysteresis, to be greater than the former; and the difference being expressed as a fraction of the extension produced by the maximum load, values were obtained ranging from $\frac{1}{30}$ in the case of high carbon steel, to $\frac{1}{300}$ in the case of an iron wire in the hard-drawn state, or $\frac{1}{333}$ with mild steel wire annealed and then hardened by stretching. The hysteresis shown at half the range of stress in the cycle described above (Curve 8, Diagram VI.) is about $\frac{1}{2}$ of the extension produced by the maximum load of 40 tons per square inch.

In order to see how far the hysteresis in the relation of strain to stress exhibited by recently overstrained iron is statical in character, or how far it depends on the rate of loading, a cycle was performed allowing ten minutes to elapse after the addition of every 4 tons of stress. The only effect was to produce a series of little notches in the curve obtained, similar to the notch shown at the stress of 34 tons in Curve 7, Diagram VI. The area of the cycle was thus not appreciably affected. The time allowed after the addition of every 4 tons was ample so far as the amount of creeping was concerned, as is clearly shown by the creeping at the stress of 20 tons in Curve 7, Diagram VI. If a much longer time had been allowed to elapse, then recovery of elasticity would have taken place as in Curves 3 and 7, Diagram VI., and the question of the static character of the hysteresis would have become complicated.

The back creeping which occurs after the removal of the load from a specimen which has been several times overstrained (for example, the creeping shown to have occurred during 5 minutes in Curve 8, Diagram VI.) is not simply due to the immediately preceding loading, but to all previous loadings. It was often observed that if sufficient time were allowed to elapse after the removal of a load, the zero reading would become negative. That is, the bar would become shorter than it was before the loading was commenced—an effect which is no doubt to be ascribed to previous overstrains, and is analogous to phenomena which have been observed in the residual charge of dielectrics, and in the torsional strains of glass and other materials.

Before leaving this section of the paper, attention should be called to the close analogy between the hysteresis effects shown in Diagram VI., and the known characteristics of magnetic hysteresis in iron.†

* "On Hysteresis in the Relation of Strain to Stress," 'B.A. Report,' 1889, p. 502.

† EWING. "Experimental Researches in Magnetism," 'Phil. Trans.,' 1885, or book on "Magnetic Induction in Iron and other Metals."

boiling water for many hours, and another was kept in a sand bath at about 250° C. for half an hour or so ; in neither case was there found, on cooling, any change in the elastic condition of the material.

In Diagram No. VII. there is shown the history of a specimen which was dipped in boiling water, whenever an overstraining load had been applied and removed. By this means recovery from overstrain instead of taking days, as in Diagram No. III., was effected in a few minutes. The material and the primary overstrain given to it are exactly as in the second example of slow recovery with lapse of time given above ; so that Curves Nos. 1 and 2 of this diagram (No. VII.) should be practically the same as Nos. 1 and 2 of Diagram IV. In order to show that the two pairs of curves are really to a close approximation identical, some of the extensometer readings taken to obtain these curves are compared in the following table. Curve No. 2 in both cases represents the first loading performed after the overstrain which is illustrated by Curve No. 1.

Load in tons/in ² .	Curves No. 1.		Load in tons/in ² .	Curves No. 2.	
	Diagram IV.	Diagram VII.		Diagram IV.	Diagram VII.
0	0	0	0	0	0
8	241	240	8	259	258
16	482	483	16	539	536
20*	604	606	24	830	829
24	810	825	32	1171	1167
28	1440	1430	35	1349	1335
29	out of range	(say 6500)			
35					

The readings for the other curves of Diagram VII. need not be tabulated.

Immediately after the readings for Curve No. 2, Diagram VII., were obtained, the specimen was taken out of the testing machine and placed in a bath of boiling water for 4 minutes. It was then removed, cooled in cold water and re-tested by gradually applying a load of 35 tons per square inch. Curve No. 3 was plotted from the observations taken. This curve is very similar to Curve No. 5 of Diagram IV., and is distinctly straighter than Curve No. 4 of that diagram ; so that 4 minutes at 100° C. has sufficed to produce more perfect recovery than would have resulted from, say, a fortnight's rest at the ordinary laboratory temperature.

After having been thus recovered and tested, the specimen was turned down in the centre to avoid breaking in the machine grips. About 4 inches at each end were left at the full diameter of 1 inch, a central portion, fully 9 inches long, being turned down to about 0·8 of an inch, and gradually tapered out at each end to the full

* Here elastic behaviour may be said to end.

diameter. On now testing the specimen, no change was found in the behaviour of the material; Curve No. 4, which shows this test, agreeing very accurately with Curve No. 3 up to the stress of 35 tons per square inch. This maximum load of 35 tons to the square inch (now 17.50 tons total instead of 26.91 tons as before turning down) was kept on for 1 hour, with the result that slight creeping took place, as is shown in Curve No. 4. On augmenting the load a distinct yield-point was got at $37\frac{1}{2}$ tons per square inch. This second yield-point happened at a lower stress than would naturally have been expected, for in Diagram No. IV. the same material is shown to have been subjected to a stress of over 40 tons per square inch without a second yield-point having been passed. The lowness of the yield-point in the present case, was probably due to an inherent weakness in the specimen, which was shown by the small flaw which ran up the centre of the bar.* Owing to the specimen having been turned down this weakness would exert a greater influence than when the bar was of the full diameter of 1 inch. Experiments on another specimen of the same material, in fact, directly showed that after turning down a yield-point was obtained, at a stress lower than that to which the specimen had already been subjected without other than elastic yielding resulting. Such behaviour was anomalous. With other material which exhibited no flaw, turning down was found to have no effect on the position at which subsequent yielding took place.

The second yield-point shown in Diagram VII. having been passed, the material was once more in the semi-plastic state, so to effect recovery it was placed in boiling water again for 10 or 15 minutes. On cooling and re-testing, a third yield-point was obtained at $41\frac{1}{2}$ tons per square inch, as is shown by Curve No. 5, Diagram VII. The specimen was once more put in boiling water and then tested, with the result that fracture occurred at a stress of 50 tons per square inch. The break was outside the central 8-inch length, close to the tapering neck joining turned and unturned portions.

A short virgin specimen of the same rod as the above was tested (after being turned down in the centre to a diameter rather smaller than in the last case), in order to find the ordinary ultimate strength of the material. The result of this test has already been given on p. 4; local extension set in at a stress of 39 tons per square inch of original area, or about 45 tons per square inch of actual stress, and fracture was allowed to occur at that load.

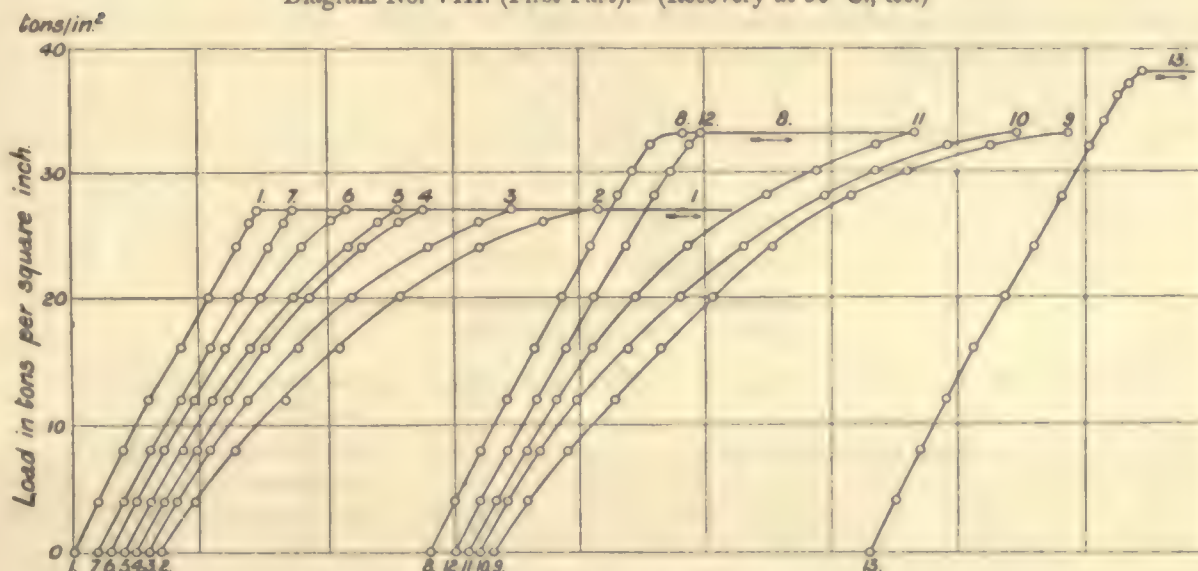
The effect which a temperature of 100° C. had in hastening the recovery process was further strikingly shown by an experiment on one of the specimens employed to obtain Diagram V. This specimen had been allowed to rest for three and a-half months, and was even then found to exhibit considerable imperfection of elasticity. By heating to 100° C. for a few minutes, a marked improvement was made in the elastic behaviour of this specimen.

* See pp. 4 and 14.

Effect on Recovery of Temperatures below 100° C.

Diagram No. VIII., which is in two parts, gives the complete history of a specimen which was allowed to recover its elasticity at various temperatures, after having been overstrained. It shows, among other things, the very considerable hastening produced in the process of recovery from overstrain by even such a moderate temperature as 50° C. (120° Fahr.). A lengthy description of this diagram need not be given, as the side-notes accompanying the diagram give all necessary details. The tables which follow give most of the readings from which the curves of this diagram have been plotted. The material employed differed slightly from that considered last, particularly as regards the position and character of the yield-point; it resembled more closely, perhaps, the material of Diagram III.

Diagram No. VIII. (First Part).—(Recovery at 50° C., &c.)



Extensions - diminished as explained on page 12.

Scale:—1 unit = $\frac{1}{1000}$ of an inch. 2 — 1 — 3

Curve No. 1.—Primary test.

" " 2.—30 minutes after No. 1.

" " 3.—After 5 minutes at 50° C.

" " 4.—" 15 " more at 50° C.

" " 5.—" 17 hours at normal temperature (say 13° C.).

" " 6.—After 15 minutes at 50° C.

Curve No. 7.—After 5 minutes at 95° C.

" " 8.—3 days after No. 7.

" " 9.—20 minutes after No. 8.

" " 10.—4 hours after No. 8.

" " 11.—After 15 minutes at 50° C.

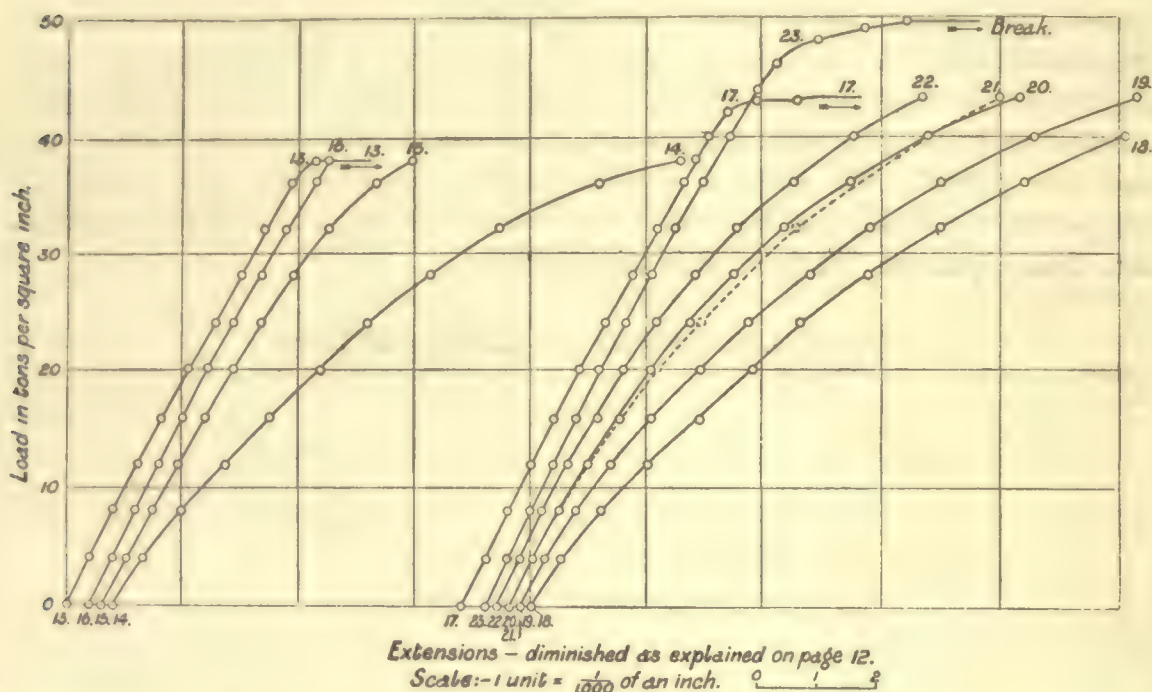
" " 12.—" 15 " " 70° C.

" " 13.—" 5 " " 95° C.

A comparison of the distances at the top between Curves 3, 4, 5, and 6, strikingly indicates the large effect of a small increase in the temperature of the restoring bath. The distance between 3 and 4 (after subtracting $\frac{1}{3}$ th of a unit for change of origin), i.e., $1\frac{1}{3}$ units, may be taken as a measure of the recovery due to 15 minutes

at 50° C. Similarly, only $\frac{1}{3}$ th of a unit (the distance between 4 and 5) measures the recovery due to 17 hours at the normal temperature (about 13° C.), while $\frac{3}{5}$ ths gives the recovery due to a further 15 minutes at 50° C.

Diagram No. VIII. (Second Part).—(Recovery at 60° C., &c.)



Curve No. 13.—See first part of diagram.

" " 14.—20 minutes after No. 13.

" " 15.—After 15 minutes at 60° C.

" " 16.— " 10 " " 95° C.

" " 17.— " specimen turned down.

" " 18.—20 minutes after No. 17.

" " 19.—After 5 minutes at 60° C.

Curve No. 20.—After other 15 minutes at 60° C.

" " 21.—After 16 hours at normal temperature.

" " 22.—After 15 minutes at 60° C.

" " 23.— " 10 " " 95° C.

Comparison of Curves Nos. 19, 20, 21, and 22, which illustrate the process of recovery after the passage of the fourth yield-point, shows a similar large difference between recovery at the ordinary temperature and that at 60° C. (140° Fahr.). In this case Curve No. 21 (obtained 16 hours after No. 20) shows that the material has yielded more, after its long rest, except for the higher loads. This apparent weakening is, of course, not due to the resting, but to the fact that the re-application of the load, necessary to obtain the readings for Curve No. 20, has had the effect of further overstraining the material to a slight extent. A curve obtained immediately after No. 20 would have fallen below that curve and also below Curve No. 21, while reaching approximately the same top point as No. 20. It may here be remarked that all the curves of this diagram have been obtained from first loadings

READINGS for Diagram No. VIII. (First Part.)

Load in tons/in ² .	Curve 1. (first test).	Curve 2. (30 minutes after 1.)	Curve 3. (5 minutes at 50° C.)	Curve 4. (15 minutes at 50° C.)	Curve 5. (17 hours at 13° C.)	Curve 6. (15 minutes at 50° C.)	Curve 7. (5 minutes at 95° C.)
0	0	0	0	0	0	0	0
4	119	126	122	122	122	120	120
8	239	258	248	248	247	242	241
12	360	397	377	371	370	366	366
16	486	539	517	500	499	489	489
20	608	688	660	635	633	619	611
24	729	850	820	776	777	750	734
26	789	952	910	857	849	822	798
27	820 and then off scale	1019	960 } 965 }	901 } 905 }	889 } 890 }	860	828
20	...	800	745	685	670	646	612
10	...	459	405	360	348	330	308
0	...	63	27	19	4	1	-1

Load in tons/in ² .	Curve 8. (3 days after 7.)	Curve 9. (20 minutes after 8.)	Curve 10. (4 hours after 8.)	Curve 11. (15 minutes at 50° C.)	Curve 12. (15 minutes at 70° C.)	Curve 13. (5 minutes at 95° C.)
0	0	0	0	0	0	0
4	120	128	120	122	120	120
8	240	260	248	248	241	240
12	361	398	379	371	365	360
16	482	534	518	500	489	482
20	605	675	661	636	611	607
24	729	822	811	779	738	729
28	850	986	974	940	860	850
30	911	1079	1064	1029	924	910
32	978	1195	1170	1126	989	971
33	1028 and then very large yielding	1290	1250	1180	1022	1001
						tons in ² .
20	...	869	829	761	627	34 1032
						36 1094
10	...	520	478	419	318	37 1128
0	...	99	79	35	10	38 1163
						and then large yielding

READINGS for Diagram No. VIII. (Second Part.)

Load in tons/in ² .	Curve 13. (See last table.)	Curve 14. (20 minutes after 13.)	Curve 15. (15 minutes at 60° C.)	Curve 16. (10 minutes at 95° C.)	Curve 17. (After turning down.)
0	0	0	0	0	0
4	120	128	122	120	120
8	240	260	245	240	240
12	360	398	368	360	360
16	482	536	490	480	481
20	607	678	613	602	601
24	729	820	739	726	724
28	850	973	865	849	849
32	971	1133	997	970	970
36	1094	1320	1138	1094	1092
38	1163 and large yielding	1440 } 1450 }	1219	1157	1152
30	...	1190	970	910	tons/in ² . 40 1212
20	...	853	662	608	42 1280
10	...	492	347	303	43 1330
0	...	78	17	- 3	1365 } 43½ large yielding

Load in tons/in ² .	Curve 18. (20 minutes after 17.)	Curve 19. (5 minutes at 60° C.)	Curve 20. (15 minutes at 60° C.)	Curve 21. (16 hours at 15° C.)	Curve 22. (15 minutes at 60° C.)	Curve 23. (10 minutes at 95° C.)
0	0	0	0	0	0	0
4	128	122	122	122	120	120
8	261	249	247	247	240	239
12	402	380	370	371	363	360
16	547	515	498	499	488	480
20	691	657	624	629	610	600
24	832	798	759	768	741	722
28	989	950	895	907	871	845
32	1150	1100	1039	1049	1009	966
36	1320	1260	1195	1207	1158	1089
40	1508	1439	1359	1360	1308	1212
43½	1712	1612	1518	1500	1445	...
20	911	820	758	739	700	tons/in ² . 44 1336
0	100	38	24	19	8	46 1402
						48 1488
						49 1550
						49½ 1598
						and then large yielding and fracture

of the specimen at the various stages, so that, as explained when Diagrams Nos. V. and VI. were described, cyclic conditions of material are not represented. The difference between the behaviour of the material when a gradually increasing load was applied for a first time, and when the same load was applied for a second time, was, however, not usually so great as that shown in Curve B, Diagram V., at least with regard to the yielding at the higher loads. At early stages in recovery slightly smaller elongations were obtained on a second loading, but at intermediate stages greater extensions were obtained at the lower loads, and approximately the same extensions at the higher. The following table of extensometer readings, obtained from a specimen very similar to the last, may be taken as showing maximum differences, for the material commonly employed in these experiments, between the elongations produced at intermediate stages in recovery by a first and by a second loading. Curves Nos. 6 and 6' of Diagram IX. also show in a striking fashion this difference in elastic condition.

Load in tons/in ² .	Extensometer readings.					
	1st application.	2nd application.	Difference.	1st application.	2nd application.	Difference.
0	0	0	0	0	0	0
4	120	120	0	120	120	0
8	246	246	0	240	246	+ 6
12	368	370	+ 2	362	370	+ 8
16	490	501	+ 11	488	500	+ 12
20	619	638	+ 19	618	637	+ 19
24	759	779	+ 20	760	776	+ 16
28	930	936	+ 6	917	925	+ 8
28½	961	959	- 2	939	945	+ 6

The effect produced by a third loading of a specimen usually differed from that produced by a second, but the difference was comparatively very slight.

To return to Diagram No. VIII., in the last test of the specimen (illustrated by Curve No. 23 in the second part of the diagram), the load was increased by a quarter of a ton to the square inch at a time; a gradual falling away from elastic behaviour was recorded, and finally local extension and fracture occurred at a stress of $49\frac{1}{2}$ tons per square inch. This corresponded to about 46 tons per square inch of primitive area. The total elongation which the specimen had received was estimated to be 12 per cent. on an 8-inch length.

A fresh specimen from the same rod as the above, broken in a single test without allowing intermediate recoveries to take place,* gave an ultimate strength of rather

* Owing to the specimen breaking in the machine grips (at a stress of 38 tons to the square inch) a partial recovery took place while the specimen was turned down in the centre. The strength given above may therefore be a little too great and the elongation a little too small.

under $40\frac{1}{2}$ tons per square inch of original area. The total elongation in this case was found to be fully 16 per cent. on the 8-inch length.

In order further to call attention to one or two features of this recovery from overstrain and the effect of temperature on it, the history of another specimen is given in Diagram No. IX.

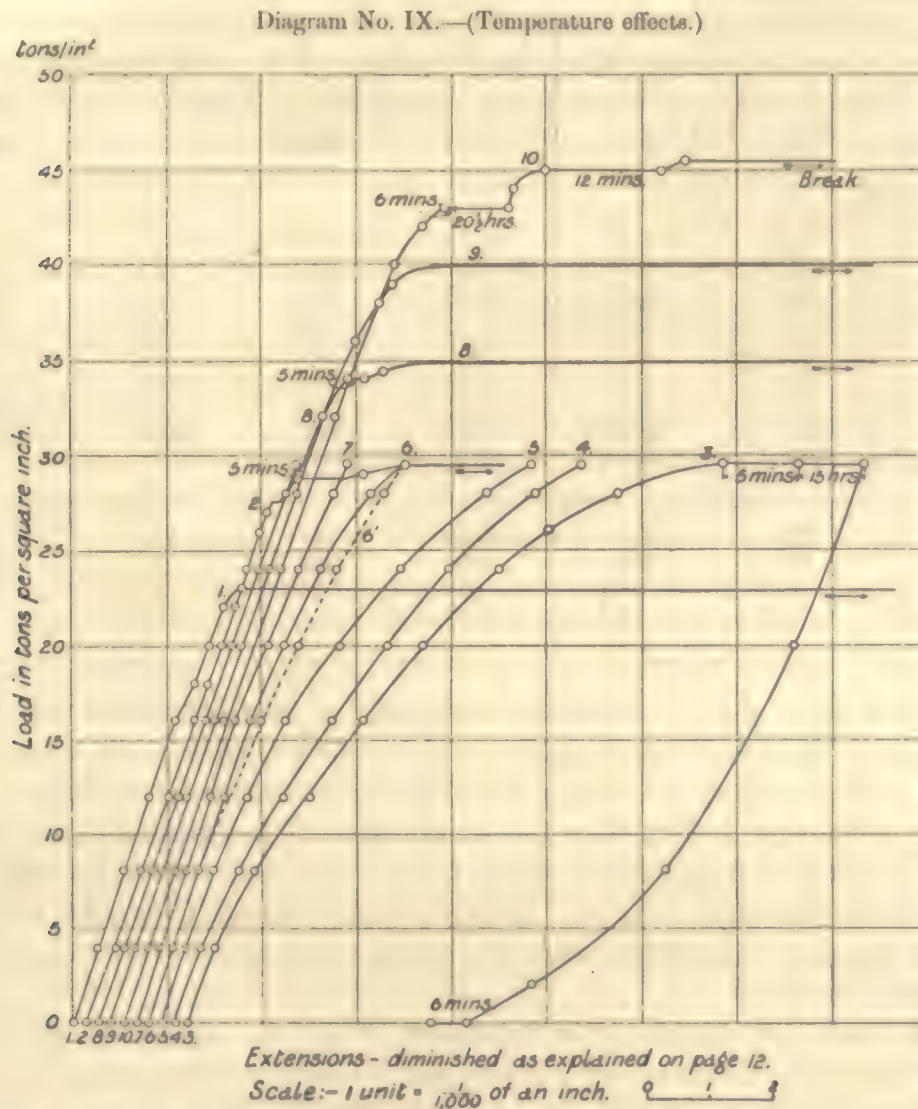
The steel rod from which this specimen was cut differed but slightly from preceding ones. The rod was 1 inch in diameter, but the specimen was turned down, except at the ends, to a diameter of about 0·8 of an inch. The yield-point occurred at a stress of 23 tons per square inch, and was well defined like those shown in Diagrams III. and VIII., unlike those in Diagrams IV. and VII. The position of the yield-point was, however, sometimes found to vary even with specimens taken from the same rod. Thus, the specimen of the present diagram (No. IX.) gave apparently a perfectly steady extensometer reading after 22 tons per square inch had been applied—steady for, say, half a minute. The addition of the next half-ton produced rather greater elongation than was in accordance with the elastic law, but the reading was still steady. With 23 tons, however, creeping set in shortly after the extensometer reading—a rather large one—had been observed. This yielding continued, becoming greater and greater, and the skin of oxide began to spring off in the manner characteristic of the yield-point. Another specimen taken from the other end of the same bar (a 10-foot one) showed creeping and the springing off of the oxide after 22 tons of stress had been applied.

After the passage of the yield-point, illustrated in Curve No. 1, Diagram IX., the specimen was put into boiling water, and kept there for over 12 hours. This was to see if the position of the second yield-point would be affected by such prolonged treatment. As was expected, on cooling and re-testing the specimen a yield-point occurred at a load which agreed with that obtained from an adjacent specimen of the same rod, which had been immersed in boiling water for 3 minutes only. A third specimen from this same rod, after being overstrained, was put in a sand-bath, and kept at 250° C. for half-an-hour. On slowly cooling and then re-testing, the material behaved exactly as in the case of the comparison specimen, which had been restored by 3 minutes' immersion in boiling water. Had the specimen been annealed by heating to redness and slowly cooling, then, of course, the effect of overstrain would have been entirely annulled, and a yield-point obtained at a load corresponding to the stress at which the primary yield-point occurred.* It was found, however, that no effect (other than the recovery from the temporary effect of overstrain) was produced, until a fairly high temperature was attained.

To return to Diagram No. IX. After the second yield-point had been passed, the bar was re-measured and re-tested in the usual manner, Curve No. 3 being obtained. In this test the maximum load was kept on over night, and the creeping which

* See paper by UNWIN, "On the Yield-point of Iron and Steel, and the Effect of Repeated Straining and Annealing," 'Roy. Soc. Proc.,' vol. 57, 1895.

occurred during the first 5 minutes is shown to have been considerable; for the next 15 hours it was perhaps not so great as might have been expected. This creeping went to the production of permanent set. Curve No. 4, Diagram IX., was obtained



Curve No. 1.—Primary test.

" " 2.—After 12 hours at 100° C.

" " 3.—15 minutes after No. 2.

" " 4.—After load removed from 3.

Specimen now at 45° C., see table, p. 32.

Curve No. 5.—After 3 minutes at 60° C.

Curve No. 6.—After 4 minutes at 70° C.

" " 6'.—Immediately after No. 6.

" " 7.—After 4 minutes at 70° C.

" " 8.— " 3 " " 100° C.

" " 9.— " process A, diagram X.

" " 10.— " " B, " X.

immediately after the removal of the load from the test illustrated by Curve No. 3, and then the specimen was kept at 45° C. for 5 minutes, and afterwards for 15 minutes. The effects produced—which were slight—are shown in the following table. The

second column under each heading in that table gives the extensometer readings for a test performed immediately after that given in the preceding column.

Load in tons/in ² .	Extensometer readings.					
	Curve No. 4, Diagram VIII.		After 5 minutes at 45° C.		After 15 minutes at 45° C.	
	1st.	2nd.	1st.	2nd.	1st.	2nd.
0	0	0	0	0	0	0
4	121	122	120	121	120	120
8	251	251	242	249	241	245
12	387	388	378	384	369	378
16	525	521	519	520	503	511
20	670	662	661	661	650	658
24	818	812	818	814	802	808
28	987	979	988	981	978	969
29½	1059	1048	1061	1049	1050	1039
¼ minute (say)	1061	1050	1070			
20	762	749	766	751	755	739
8	348	336	350	339	339	324
0	22	14	25	20	29	14
½ minute (say)	19	10	20	

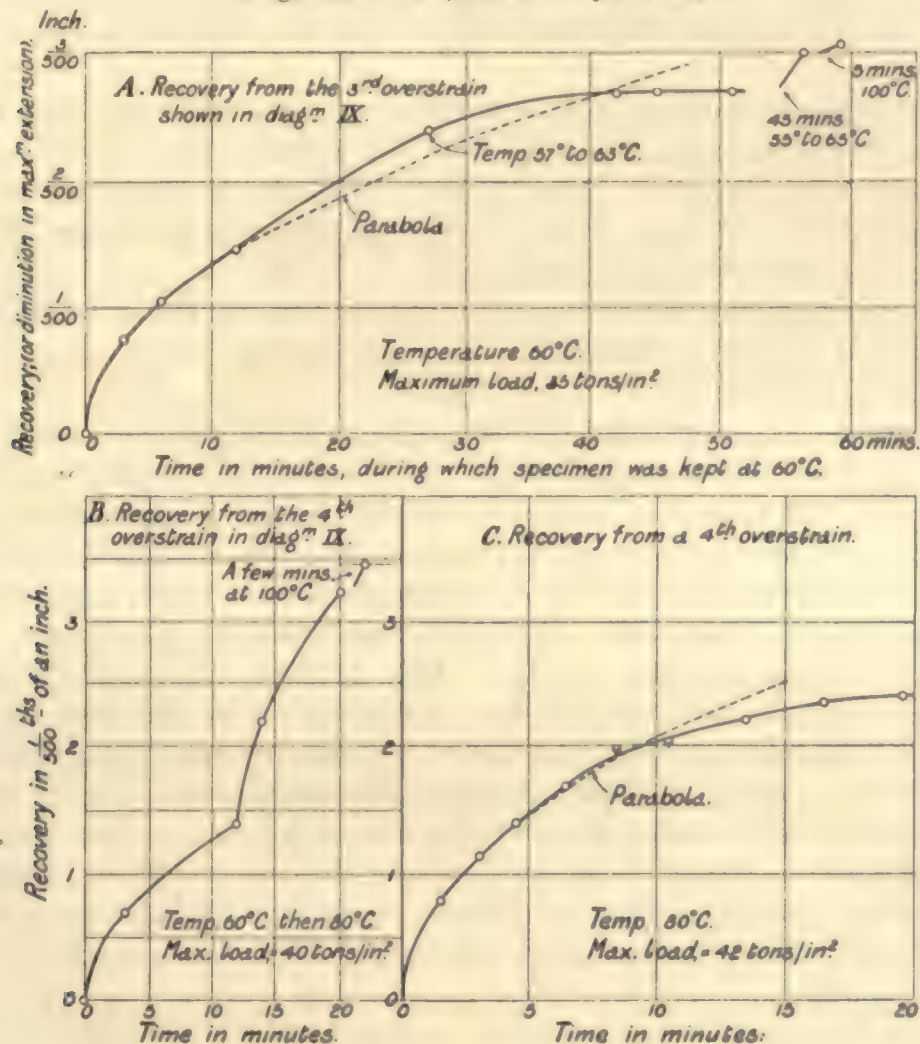
These figures show that an immediate re-application of the load has produced in each of the three cases less total elongation than the first application, in consequence of the bar's gradual settlement into a cyclic state through successive loadings. After the recovery has become fairly perfect, this considerable diminution in the total elongation obtained by a second application of the testing load does not occur. This was clearly shown in the table on p. 29. In the present diagram Curve No. 6' (shown dotted) was obtained immediately after No. 6, and it shows almost no change in the total elongation produced.

The tests made immediately after treatment at 45° C. are shown by columns 2 and 3 of the table above to have given slightly greater total elongations than those obtained from the loadings performed immediately before warming. This is perhaps contrary to what might have been expected, since increase of temperature has been shown to hasten recovery. But although the total elongations are greater, the process of recovery really has been aided. This is shown by the fact that distinctly smaller yieldings are obtained with low loads after the bar has been heated to 45° C. But though the bar is more perfectly elastic under low loads, under higher ones the yielding which occurs has not been decreased; so that, as the specimen is subjected to a gradually increasing load, there is a transition from more elastic behaviour to less, which is suggestive of a yield-point.

To return again to Diagram No. IX., the specimen, after being warmed to 45° C. in

the manner just explained, was subjected to the treatment recorded in the notes accompanying the diagram, and finally, as shown by Curve No. 8, complete restoration of elasticity was effected. The load was therefore increased until a yield-point was obtained at a stress of about 35 tons per square inch. The recovery from the overstrain produced by the passage of this third yield-point is shown by means of a curve at A in Diagram No. X. This curve was obtained by plotting amounts of recovery—

Diagram No. X.—(Time-recovery Curves.)



measured in the manner described on page 25 (that is, by the diminutions in the extensions produced by the maximum load)—against the time taken at 60° C. to produce the recoveries. This method of measurement is of course faulty, for it has been shown above that a slight recovery may have occurred, although a greater total elongation has been obtained. But if the recovery is tolerably rapid, the method may be justified, for the sake of comparing the rates of recovery at different stages of completion, by means of a time-recovery curve. At C, Diagram X., there is shown a

curve of this kind obtained from a specimen whose history will not be given. This curve was more fully and carefully determined than those obtained from the specimen of Diagram No. IX.; but any of the curves in Diagram No. X. show that in the earlier stages the amount of recovery is approximately proportional to the square root of the time.

The heating of the specimens was accomplished by immersing in a hot water-bath at the required temperature for the required time, and then cooling by at once dipping in cold water. Had the specimen been allowed to cool slowly in the air, then greater recovery, due to a long and indefinite time at lower temperatures, would have been obtained.

Curve A, Diagram X., shows that at 60° C. a long time would have been required to produce perfect recovery, so the specimen (of Diagram IX.) was finally put in boiling water for 5 minutes. After cooling, a gradually increasing load was applied, and a fourth yield-point obtained at a stress of 40 tons per square inch. This test is shown by Curve No. 9, Diagram IX.

The recovery from this fourth overstrain is illustrated by Curve B, Diagram X. First 60° C. and then 80° C. were employed, perfect recovery being again obtained by bringing the piece to 100° C.

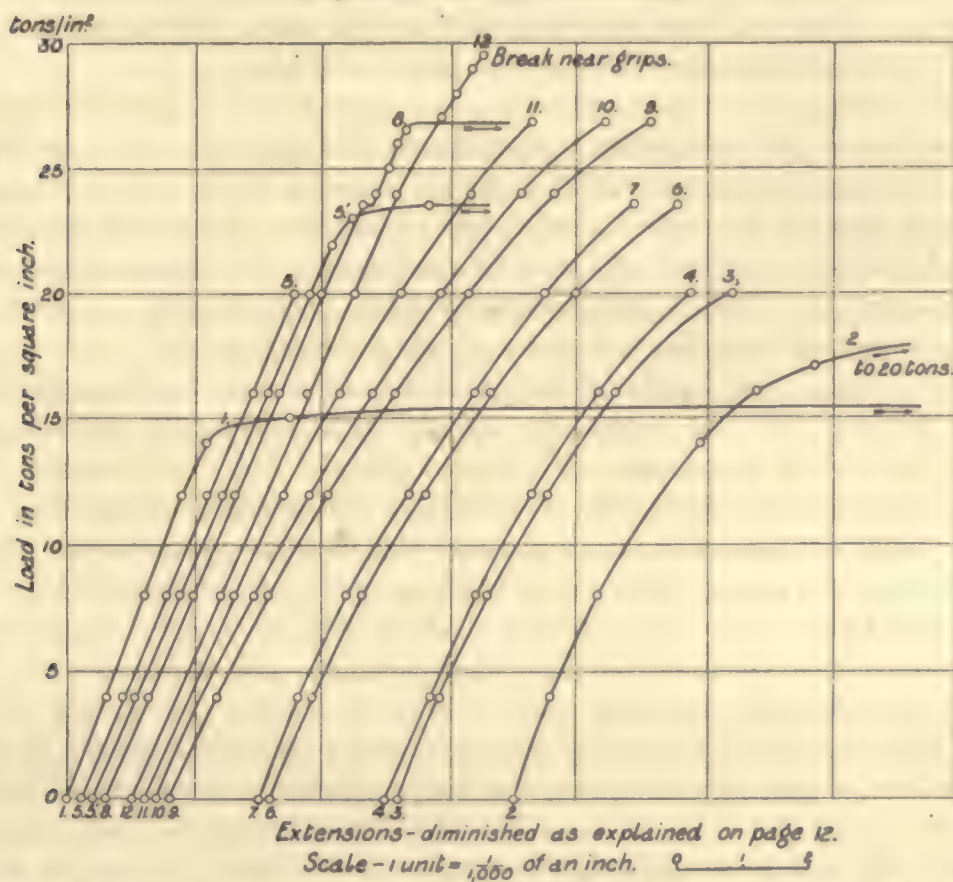
On load being once more applied to this specimen, elastic behaviour was shown up to the stress of 40 tons per square inch. At the 43rd ton, creeping was detected, and this load was allowed to remain on for 20½ hours. Considerable extension resulted, as is shown by Curve 10, Diagram IX. On now further increasing the load, the yielding was found for the subsequent three half-tons to be in close accordance with the elastic law. With the fourth half-ton (*i.e.*, at 45 tons per square inch) creeping was again detected. After 12 minutes, however, this creeping became very slow, so another half ton was applied, with the result that local extension and fracture occurred at that load of 45½ tons per square inch. This stress was equivalent to rather over 42½ tons per square inch of primitive area; the total elongation was about 0·81 of an inch, or rather over 10 per cent. on the 8-inch length.

A virgin specimen from an adjacent portion of the same bar as the above, gave, when tested at once to breaking, an ultimate strength of 36½ tons per square inch of original area; the total elongation in this case was 1·82 inches or nearly 23 per cent. on the 8-inch length.

It will be noticed that the distance in tons between the successive yield-points shown in Diagram IX. is roughly constant, and further that fracture has occurred where a yield-point (if not a fracture) would naturally have been expected. More correctly, it is the distance between a yield-point and the previous maximum load that is the same throughout. Thus a specimen from the same bar as that employed for this diagram, No. IX., was overstrained primarily by 27 tons to the square inch, and the subsequent yielding was obtained at 33 tons. That is at about 4 tons higher than the second yield-point shown in Diagram IX., when the primary loading was only carried to 23 tons per square inch. This regularity in the raising

of the yield-point was also shown in Diagram No. VIII., the material being slightly different from that which has just been considered; and, further, it will be shown in Diagram No. XI., which gives the history of a specimen of unhomogeneous wrought iron. The distance between the yield-points is 3 to $3\frac{1}{2}$ tons with the common wrought iron and 5 or 6 tons with the semi-mild steel usually employed in these

Diagram No. XI.—(Common iron.)



Curve No. 1.—Primary test.

" " 2.—Immediately after No. 1.

" " 3.—" " " 2.

" " 4.—" " " 3.

" " 5.—16 hours after No. 4.

" " 5'.—After a few minutes at 100° C.

" " 6.—Immediately after No. 5.

Curve No. 7.—Immediately after No. 6.

" " 8.—After a few minutes at 100° C.

" " 9.—Immediately after No. 8.

" " 10.— $\frac{1}{4}$ hour after No. 9.

" " 11.—After 5 minutes at 55° C.

" " 12.—" 10 " " 100° C.

experiments. In Diagram No. VIII. yield-points were obtained at loads of about 27, 33, 38, $43\frac{1}{4}$, and $49\frac{1}{2}$ tons per square inch,—fracture occurring at the last mentioned stress. With another specimen from the same steel rod the primary loading was carried to 30 tons per square inch, and after recovery of elasticity a 2nd yield-point was obtained at about 35 tons per square inch. On again restoring elasticity a 3rd yield-point was found to occur at a stress somewhat under 40 tons,

and when recovery from overstrain had once more been effected fracture took place at 45 tons per square inch. It is however probable since this material is the same as in Diagram VIII., that had the primary loading in the present case been carried only to 29 tons per square inch, then a yield-point would have been obtained at a stress of 44 tons, and fracture would not have taken place until a load of over 49 tons per square inch had been applied. A yield-point obtained at a high stress is thus a crisis in the history of the specimen under test; the material is in danger of giving way, but if it does not, then, after recovery it will stand, before fracture occurs, a stress 5 or 6 tons higher than that at the critical yield-point.

It should, perhaps, be pointed out that in Diagram No. VII. no uniformity exists in the position of the yield-points. In this case the specimen cannot, perhaps, be taken as illustrating the behaviour of a certain material, for it will be remembered that a small flaw ran through the centre of the bar from which this specimen was taken, and probably this flaw had a considerable influence in determining the position of the yield-points.* Chemically this material differed only slightly from that of the other steel rods used, as is shown by the analyses given on page 4.

Before concluding this section of the paper, attention should perhaps be directly called to Diagram No. XI., which has already been incidentally referred to. It gives the history of a specimen of common wrought iron, the diameter of the specimen being 1 inch. Curve No. 1 illustrates the primary loading and shows that the yield-point has occurred at a stress of $15\frac{1}{2}$ tons per square inch. After the large stretching had ceased, and the load had been removed, the 8-inch length of the specimen was found to have been stretched about 0.20 of an inch. On re-loading, the material exhibited comparatively little semi-plasticity, as is shown by Curve No. 2. The load was, therefore, increased until a stress of 20 tons per square inch was attained, the specimen being thereby stretched further by about a quarter of an inch on the 8-inch length. On re-testing, the curve obtained was still found to agree closely with Curve No. 2 up to the stress of 15 tons, but as the loading was now continued to 20 tons the semi-plasticity was more clearly shown. Curve No. 5 shows that a night's rest at the ordinary temperature has been sufficient to produce complete recovery of elasticity; so common iron recovers much more quickly than the semi-mild steel employed for the most part in the course of these experiments. It may be of interest here to recall that the half-inch specimens of comparatively mild steel, employed for Diagram No. V., recovered at a very much slower rate than the harder steel usually employed in these experiments.

After Curve No. 5 was obtained the specimen was put in boiling water for a few minutes to ensure perfect recovery. On testing, Curve No. 5 was repeated, and on increasing the load a yield-point was got at $23\frac{1}{2}$ tons per square inch, as shown by Curve 5'. Curve No. 8 shows that a few minutes in boiling water has effected perfect recovery from this second overstrain. The maximum load of $23\frac{1}{2}$ tons was kept on in this test for 45 hours, and only the slight creeping shown in the diagram occurred.

* See p. 24.

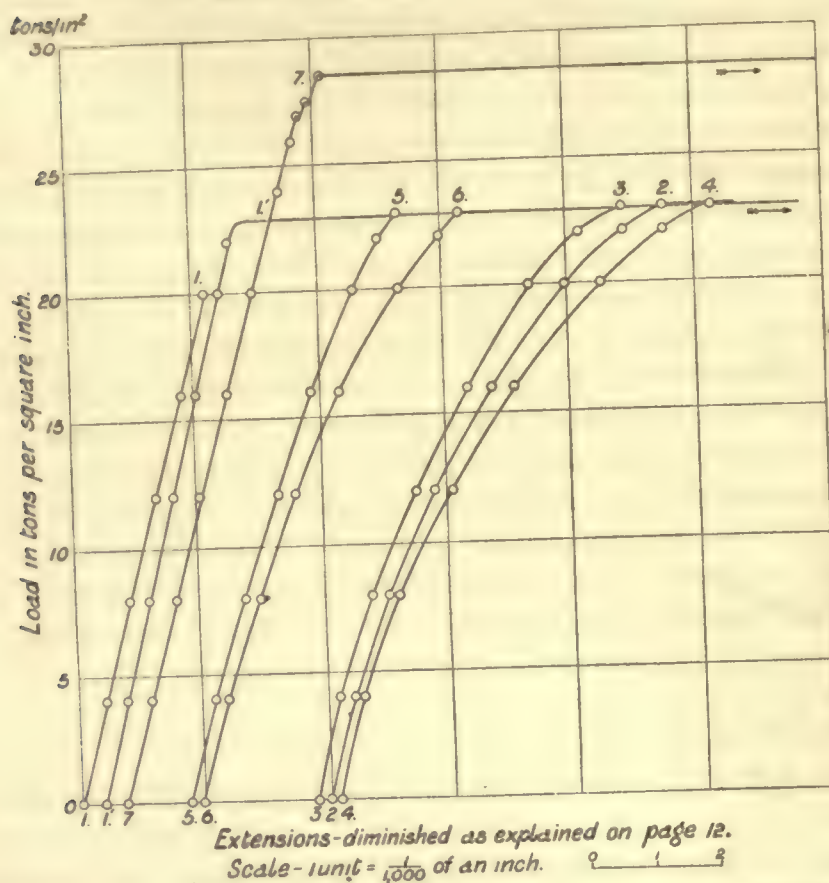
On increasing the load, a well-defined yield-point was now got at a load of $26\frac{1}{4}$ tons per square inch. Comparison of Curves Nos. 9, 10, and 11 shows the remarkable hastening in the recovery from this overstrain, produced by a temperature of 50° C.; while Curve No. 12 shows the material once more in the perfectly elastic condition. On now carefully increasing the load a fracture was obtained close to the upper machine grips, at a stress of $29\frac{1}{2}$ tons per square inch. The specimen was gripped and loaded again, with the result that fracture occurred close to the lower grips at $29\frac{3}{4}$ tons per square inch. This was repeated a third and a fourth time, so that the occurrence of the fracture close to the grips was not due to a primary effect of the gripping, that is, it was not due to the gripping having prevented the material from becoming hardened by overstrain. The breaking load, of over $29\frac{1}{2}$ tons per square inch, was equivalent to a stress of fully 27 tons per square inch of the original area of the specimen. Another specimen of the same rod was found to give a yield-point at 14 tons per square inch, and on steadily increasing the load fracture occurred, near the centre of the specimen, at slightly under 23 tons per square inch of original area. The elongation was about 21 per cent. on an 8-inch length. Common iron thus exhibits the same features as steel in respect of recovery from overstrain and the effect of temperature on it; but in the case of common iron recovery is comparatively rapid.

The Effect of Mechanical Vibration on Recovery from Overstrain.

Diagram No. XII. illustrates the effect of mechanical vibration on recently overstrained iron, and shows that such treatment has an opposite effect to that of increase of temperature—instead of the recovery process being hastened, the material is made distinctly less elastic. The following table gives most of the figures from which various curves of this diagram have been plotted. The material employed is the same as that used for Diagram No. IX., but the specimen in this case was not turned down, and so was of the full diameter of 1 inch throughout its length.

Load in tons/in ² .	Curve No. 1. (2nd—after vibrating.)		Curve No. 2.	Curve No. 3. ($\frac{1}{2}$ hour's rest.)	Curve No. 4. (After vibrating.)	Curve No. 5. (16 $\frac{1}{2}$ hours' rest.)	Curve No. 6. (After vibrating.)
	1st	2nd				(2nd loading)	
0	0	0	0	0	0	0	0
2	60	60	61	60	59	60	60
4	122	120	122	120	119	121	120
6	182	181	188	187	185	185	185
8	245	240	251	249	251	248	249
10	307	300					
12	368	361	390	387	396	374	379
14	429	421					
16	489	482	539	529	545	502	518
18	549	544					
20	609	601	699	680	718	639	665
22		659	797	771	818	709	749
23		Off the scale	851 } 10 1008 } mins.	825 } 3 840 } mins.	868 } 10 919 } mins.	745 } 3 750 } mins.	790

Diagram No. XII.—(Mechanical vibration.)



Curve No. 1.—Illustrates primary loading.

" " 1'.—Is after mechanical vibration.

" " 2.—Immediately after No. 1'.

" " 3.—½ hour after No. 2.

Curve No. 4.—After mechanical vibration.

" " 5.—A 2nd loading, 16½ hours after No. 4.

" " 6.—After mechanical vibration.

" " 7.— " 4 minutes at 100° C.

Before the experiment corresponding to Curve No. 1 was performed, a test was made to ensure that such vibration as was contemplated would have no effect on the elastic properties of the primitive material. The specimen was loaded till a stress of 20 tons per square inch was attained, and the load was then removed. The extensometer readings obtained are shown in the first column of the table given above. The specimen was then taken out of the testing machine and vigorously tapped with a hammer, so as to make it ring in various modes. It was then re-tested and the second column of readings shown above was obtained. These readings are slightly less than those obtained during the first loading, but this was to be expected on a second loading, though, perhaps, to scarcely so great an extent. Large yielding occurred during this test at 23 tons per square inch, which is the known yield-point of the material. Hence violent vibration may be said to have had no effect on the primitive material, or if it had a slight effect, it was shown in the annihilation of the causes of small departures from accurate obedience to the elastic law.

Curve No. 2 of Diagram No. XII. shows the specimen to be in the ordinary semi-

plastic condition produced by overstrain, and Curve No. 3 the condition of the material after half-an-hour's rest. After this test the specimen was taken out of the testing machine and vigorously tapped with a hammer. On re-testing Curve No. 4 was obtained, which shows that not only has the effect of the half-hour's rest been annulled by the vibration, but that the material was rather more plastic than it had been immediately after overstrain. The specimen was next allowed to rest for $16\frac{1}{2}$ hours and was then re-tested, Curve No. 5 showing the progress made towards recovery. The specimen was then taken out of the testing machine, and once more struck with the hammer so as to make it ring. On again testing, the elasticity was found just as before to have been made more imperfect, Curve No. 6, which illustrates this test, lying below No. 5. The specimen was then put in boiling water for a little, and Curve No. 7 shows that recovery was complete. Hammering was found to have no appreciable effect on the elastic condition of material whose elasticity had been thus restored.

In concluding this section it may be of interest to state that the effect of turning down the diameter of a recently overstrained specimen was to produce partial recovery of elasticity. This was in all probability due to the warming which accompanied the cutting action—the bar being heated by conduction, and only the surface subjected to severe mechanical vibration.

The Influence of Magnetic Agitation in Hastening or Retarding the Recovery of Elasticity.

The experiment which is now about to be described was made with the object of finding the effect on recovery, of magnetising and de-magnetising an overstrained specimen.

A coil ($1\frac{1}{4}$ inch diameter \times $7\frac{1}{2}$ inches long) was made which gave a field strength at the centre of about 140 C.G.S. units, when a current of 10 amperes was passing. This coil was put round a specimen and supported at the 8-inch length, to which the extensometer was to be applied.

The material used was the same as that of Diagrams IV. and VII. ; the specimen, however, was not in its virgin condition, it had been largely overstrained and had recovered its elasticity again, so that a yield-point was not expected till a stress of about 40 tons was attained. During the loading of the specimen, a current of 10 amperes was passed at intervals through the coil, and it was found that the extensometer could clearly detect (when the current was passed) the slight elongation due to magnetisation. This elongation occurred only at the lower loads ; at the higher ones the slight contraction, which is known to occur, was quite readily observed.*

At a stress of $40\frac{1}{4}$ tons per square inch a yield-point was obtained, and while the bar was stretching rapidly at this load the current was put on and off several times, its direction being constantly reversed. The contraction, which had been noticed just before the yield-point had been reached, was still clearly shown at each "make," by

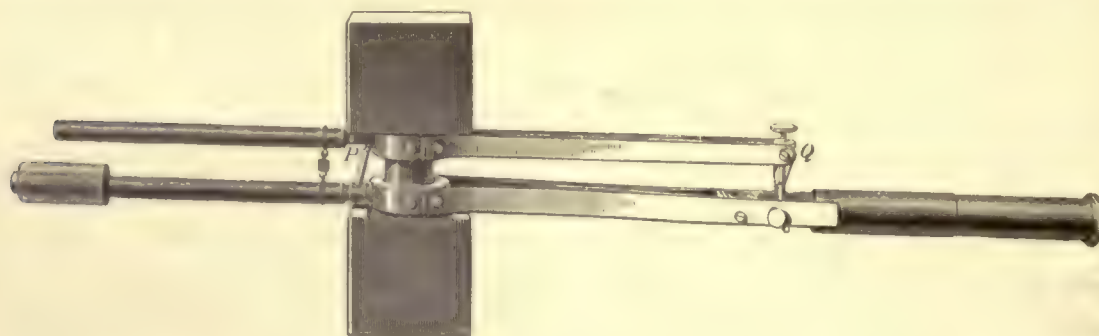
* For the change in length caused by magnetisation, when iron is under various stresses, see papers by SHELFORD BIDWELL, 'Phil. Trans.,' A, 1888, and 'Roy. Soc. Proc.,' 1890.

a temporary check in the rate of extension. Time readings—of a few minutes duration—taken while the bar was stretching, detected no change in the rate of extension when the current was allowed to pass for some time, and so the bar for that time kept magnetised.

When the stretching at the yield-point had practically ceased, the specimen was re-measured and the curve showing semi-plasticity obtained. The specimen was then allowed to rest for two hours, and the recovery effected was recorded by a curve. The current was next passed through the coil for periods of from 10 to 15 minutes, and was reversed all the time rapidly by hand, so that the bar was subjected to considerable magnetic agitation. Such treatment was found to have no appreciable effect on the recovery of the specimen, the curve obtained on re-testing being almost exactly the same as that obtained after the 2 hours' rest.

Compression Experiments.

The experiments which are now about to be described illustrate the recovery of iron from tensile overstrain by means of compression tests. These tests were carried out on small cylindric blocks, $1\frac{1}{8}$ inches diameter by $1\frac{7}{8}$ inches long, compression being applied by means of the 50-ton testing machine. The small compressional strains obtained were measured by an instrument specially designed by Professor EWING. This instrument resembles in principle Professor EWING's extensometer, especially a more recent form of that instrument, and like it is self-contained, and is entirely supported by the specimen under test. A detailed description of this instrument, which is shown attached to a compression specimen in the following illustration, need

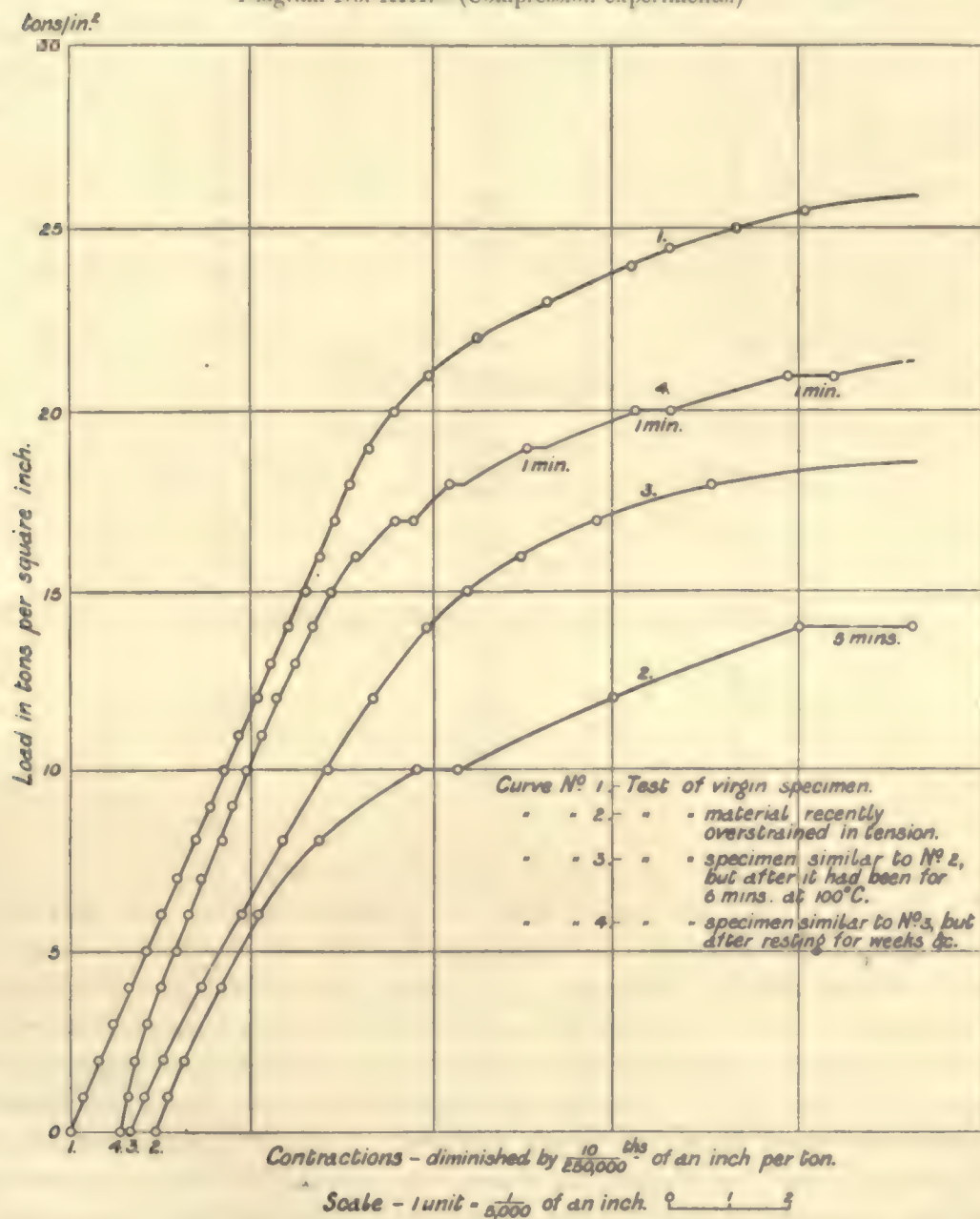


not be given here, but it may be stated that with a mechanical multiplication of 10, and further optical magnification, a contraction of $\frac{1}{250000}$ th of an inch can be measured. This corresponds to a compressional strain of $\frac{1}{312500}$ th, since the length of specimen actually tested is only $1\frac{1}{4}$ inches. It may be recalled that the unit of the readings of Professor EWING's extensometer represented an elongation of $\frac{1}{400000}$ th, the length of specimen tested being 8 inches.

The following two series of readings, obtained with the new compression instrument, clearly show by comparison the semi-plasticity which is induced in iron by

tensile overstrain. The curves which have been plotted from these readings are shown in Diagram XIII. The first series was obtained from a virgin specimen of $1\frac{1}{2}$ inch round steel rod, very similar in quality to the 1-inch rods usually employed

Diagram No. XIII.—(Compression experiments.)



in the tension experiments. The total length of the specimen was only $1\frac{2}{3}$ diameters, and the ends were carefully faced, so that "buckling" may be said to have been avoided, and the compressional stress applied in as uniformly distributed a manner as was practicable.

First Series of Compression Instrument Readings. (Test on a Virgin Specimen illustrated by Curve I. Diagram XIII.)

Load in tons per square inch.	Contractions in $\frac{1}{10000}$ ths of an inch.	Differences.
0	0	
1	20	20
2	43	23
4	88	45
6	134	46
8	183	49
10	227	44
12	277	50
14	321	44
16	367	46
18	410	43
20	468	58
21	505 }	
	time 510 }	
22	555 }	
	time 560 }	87
23	625	
24	705	150
25	800	
26	1000 }	295
	1 min. 1075 }	
The load was now removed and the following readings taken : --		
20	990	
15	915	75
10	815	100
5	705	110
1	622	
0	588	117

The difference column given above shows that the material has behaved elastically until a load of 20 tons per square inch was attained. Beyond that load there is shown a gradual but tolerably rapid departure from HOOKE'S law ; there seems to be, however, no very definite yield-point. In a tension test of this material creeping was first noticed at 23 tons per square inch, and at $24\frac{1}{2}$ tons a very large yielding occurred. YOUNG'S modulus, as calculated from the compression readings given above, was found to agree with that obtained from tension experiments to two significant figures ; in both cases the third figure was rather doubtful. Thus, the modulus as got from a first loading in tension to 20 tons per square inch, was 13,100 tons per square inch, while from a second loading to 10 tons per square inch it was found to be 13,300 tons per square inch. The modulus, as calculated from the contraction shown to have occurred in the table above, between 4 and 18 tons per square inch, is 13,600 tons per square inch.

The second series of compression instrument readings was obtained from a specimen

of the same $1\frac{1}{8}$ -inch rod, but after the rod had been overstrained largely in tension by a load of 33 tons per square inch. The compression specimen was cut from the overstrained bar immediately after the large stretching load was removed, care being taken to prevent warming during the cutting and mechanical manipulation necessary to the making of the small compression block. To test the effect of such mechanical treatment on the elastic condition of the material, a tension specimen was overstrained, tested, immediately turned down to a smaller diameter and tested again. As has already been recorded on page 39, considerable, though by no means perfect, recovery of elasticity was found to have been produced. Owing to the precautions taken in making the compression specimen used for this second series of readings, the mechanical manipulation may be assumed to have produced no effect on the elastic properties of the material.

SECOND Series of Compression Readings. (Material freshly overstrained,
Curve 2, Diagram XIII.)

Load in tons per square inch.	Contractions in $\frac{1}{250000}$ ths of an inch.	Differences.
0	0	
1	20	20
2	43	23
4	94	51
6	145	51
8	217	72
10	315	98
	time 350	
12	500	185
14	670	170
	5 mins. 768	
16	948	278
	3 mins. 1010	
18	1260	312
20	1650	
	2 mins. 1750	
	20 mins. 1835	390
Load was now removed and the following readings taken :—		
10	1615	
4	1466	
2	1415	
0	1360	

A comparison of the difference column of the present series of readings with that of the last very clearly shows the change in the elastic condition of the material, produced by tensile overstrain. There is now not even approximate conformity with HOOKE'S law at the lowest loads.

The recovery of elasticity, which is brought about either by prolonged rest at

normal temperatures, or by keeping the piece for a few minutes at a temperature such as 100°C ., is shown in the following series of compression instrument readings. This third series of readings was obtained from a compression specimen taken from the same overstrained rod as the last; but in the present case the specimen was boiled in water for 6 minutes before being tested. This test is illustrated by Curve No. 3, Diagram XIII.

THIRD Series of Compression Readings. (Showing Recovery of Elasticity produced by 6 Minutes' Boiling.)

Load in tons per square inch.	Contractions in $\frac{1}{100000}$ ths of an inch.	Differences.
0	0	
1	22	22
2	48	26
4	99	51
6	152	53
8	208	56
10	262	54
12	319	57
14	382	63
15	428 (creeping noticed)	
16	482	100
17	558	
18	660	178
19	795	
20	970 } 1 min. 1020 }	310
On removing the load the following readings were obtained:—		
15	912	
10	788	
4	639	
2	589	
0	540	

Comparison of the differences in this table and those in the last, or comparison of Curves 2 and 3 of Diagram XIII., clearly shows the large effect produced by the 6 minutes at 100°C . Comparison of the first and third series of readings, or of Curves 1 and 3, Diagram XIII., seems to indicate that the 6 minutes' boiling has not sufficed to produce quite perfect recovery of elasticity. In Curve No. 4 of this diagram—the readings need not be tabulated—there is shown the testing of a specimen very similar to that employed for Curve No. 3, but in this case it was certain that recovery was complete. The specimen was not taken from the same overstrained portion of a bar as that from which Curves Nos. 2 and 3 were obtained, but from another portion of the same material, which had been similarly overstrained. Before the compression specimen was cut off, the overstrained tension specimen had

been allowed to rest for many weeks, and had been tested and found to be quite elastic up to a stress of 35 tons per square inch. The tension specimen was, however, boiled for some time as a further precaution, and then the compression specimen was cut from it, and the test illustrated by Curve No. 4 was performed. The modulus given by this curve agrees very well with that obtained for the virgin material from Curve No. 1. The marked discrepancy shown in this curve, No. 4, at the lowest loads may evidently be discarded; it was probably due to imperfect facing of the ends of the specimen, or some such cause.

Curve No. 4, further, very clearly shows that tensile overstrain—which raises the yield-point in tension—lowers that in compression, or, it may be more definite to say, lowers the load at which any arbitrary amount of plastic contraction occurs. This is in agreement with Professor BAUSCHINGER's conclusion with regard to the elastic limits, viz., "that the elastic limit in tension cannot be raised without lowering the limit in compression, and *vice versa*."* Professor BAUSCHINGER draws a further conclusion from his experiments, namely, that when the elastic limits of a material are varied by overstrain, the range of perfect elasticity seems to remain constant, so that, if the elastic limit in tension be raised, then that in compression is lowered by an equal amount. The author's experiments do not bear this out. They show that such a proposition cannot be applied to the yield-points, for the yield-point in tension of the material in the condition whose compression properties are illustrated by Curve 4, Diagram XIII., was found to occur at a stress between 12 and 13 tons per square inch, above the yield-point of the material in the primitive condition, and no matter where the yield-points in Curves 1 and 4 be supposed to exist, the lowering, which is the result of the tensile overstrain, cannot be greater than 4 or 5 tons of stress.

The characteristics of overstrained iron in respect of hysteresis and imperfect elasticity may be considered as illustrating MAXWELL's views on the 'Constitution of Bodies,' as set forth by him in the 'Encyclopædia Britannica.'† In that article all bodies are assumed to be composed of groups of molecules oscillating about more or less stable configurations. If the oscillations are such as to cause all the groups to be continually breaking up, then we have a viscous fluid. But if "groups of greater stability are disseminated through the substance in such abundance as to build up a solid framework, the substance will be a solid, which will not be permanently deformed, except by a stress greater than a certain given stress." A solid, however, is not assumed to be entirely composed of these stable groups of molecules, or say of sensible particles, but to contain groups of less stability, and also groups which break up of themselves. When a solid has been permanently deformed or overstrained

* See UNWIN's book on 'Testing of Materials of Construction,' p. 386, or BAUSCHINGER, "Ueber die Veränderung der Elasticitätsgrenze und die Festigkeit des Eisens und Stahls," 'Mittheilungen aus dem Mech. Techn. Laboratorium in München,' 1886.

† Or see the 2nd volume of CLERK MAXWELL's 'Collected Papers.'

then "some of the less stable groups have broken up and assumed new configurations, but it is quite possible that others more stable may still retain their original configurations, so that the form of the body is determined by the equilibrium between these two sets of groups; but if, on account of rise of temperature, increase of moisture, violent vibration, or any other cause, the breaking up of the less stable groups is facilitated, the more stable groups may again assert their sway, and tend to restore the body to the shape it had before its deformation."

The semi-plasticity exhibited by recently overstrained iron may thus, on the above theory, be attributed to the less stable groups, which after overstrain are in comparative abundance. And since these less stable groups will tend to break up of themselves, there will be a slow recovery through lapse of time towards elastic behaviour which is associated with the idea of stable groups.

Increase of temperature has been shown in the present paper to hasten recovery from overstrain to a remarkable extent. This, as indicated by the quotation given above, may be ascribed to a greater facility given by slight warming, to the breaking up of the less stable groups, and possibly to the re-formation of more stable groups.

Violent mechanical vibration, however, seems to break up the rather more stable groups, rendering the material more semi-plastic and hindering the recovery process.

That recovery from overstrain, or more generally, that the phenomenon of "elastic after-action," is associated with complexity in the physical structure of the material, is further borne out by the fact that a crystalline body, such as a quartz torsion fibre, exhibits little or no after-action (in the form of zero-creeping); while a complex body like glass shows such action in marked degree. An analogy to this difference in the behaviour of material, according as it is simple or complex, is found in the phenomenon of the residual charge in the Leyden jar. Condensers with pure dielectrics such as sulphur, quartz, air, exhibit little or no residual charges; while with complex substances like glass, gutta-percha, caoutchouc, the phenomenon is particularly observable.

II. *On the Nature of Electrocapillary Phenomena. --I. Their Relation to the Potential Differences between Solutions.*

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Communicated by Professor A. W. RÜCKER, Sec. R.S.

Received January 5, --Read January 26, 1899.

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INTRODUCTION.

THE phenomenon of surface tension exhibited at the surface of separation between two homogeneous liquids may be regarded as arising from such a variation in the distribution of the matter composing each of the liquids, in the immediate neighbourhood of the surface of separation, that the energy of given quantities of the two liquids is greater when these are in the neighbourhood of the surface than when each is in the homogeneous interior of its corresponding liquid.

On such a view, the tension per unit length in the surface will be equal to dE/dS , where dE is the increase in the potential energy of the system of two liquids, resulting from an increase, dS , of the surface of separation between them. The distribution of energy here referred to may be considered independent of possible electrostatic effects at the surface of separation.

There is little doubt, however, that there is frequently a potential difference of considerable amount at the surface separating two such liquids as mercury and a solution of a salt in water. There must, therefore, be a corresponding separation of electricities of opposite sign at the surface, and we may regard these as forming a condenser-like "double-layer." This double-layer will give rise to an electrostatic surface energy, whose value we may write as $E' = \frac{1}{2}cS\pi^2$, where c is the capacity of the double-layer per unit surface and π is the potential difference across it. S is, as before, the area of the surface separating the two liquids. Now, if a small change of this surface, dS , be supposed to take place while the potential difference across the double-layer is kept constant by an external electromotive force, we get

$$dE'/dS = \frac{1}{2}c\pi^2.$$

This increase in the potential energy of the system, with increase in the surface of separation between the two components, will be an effect that tends to take place under the influence of the external electromotive force, and will be equivalent to a force per unit length tending to *increase* the surface of separation between the two liquids.

The observed surface tension will thus be

$$\gamma = dE/dS - dE'/dS = \gamma_0 - \frac{1}{2}c\pi^2,$$

where γ_0 is the surface tension arising from the non-electrical distribution of energy first mentioned. The equation will give the relation between the observable surface tension and the potential difference at the mercury surface.

The above may be regarded as the Helmholtz theory of electro-capillary pheno-

mena. LIPPMANN found that the curve showing the relation between the surface tension and the E.M.F. applied between the terminals of a capillary electrometer was (for a particular solution of sulphuric acid) approximately parabolic through a considerable portion of its course, and it appeared from this that c was a constant and that γ_0 was independent of π .

It is not a necessary consequence of considerations such as the above, that c should be constant; but if the only effect of the potential difference is to produce an electrostatic surface energy represented by $\frac{1}{2}c\pi^2$ per unit surface, then the observed surface tension should have a maximum value when $\pi = 0$, even although c may be variable. The assumption, that the maximum surface tension corresponds to zero potential difference between the mercury and the solution, has been much employed in recent years in the deduction of values for the contact potential difference between various electrodes and electrolytes. It must be remembered, however, that the observed variation in the surface tension need not be due solely to variation in the quantity $\frac{1}{2}c\pi^2$. The non-electrical surface energy, represented by γ_0 , may vary with the potential difference. A variation in the potential difference at the surface of separation between the mercury and the solution may be accompanied not only by a variation in the electrostatic surface energy, but also by a variation in the distribution of the matter in the neighbourhood of the surface.

If a variation of the kind just mentioned can be traced, it is clear that we cannot consider the phenomena as if they were due to a certain non-electrical distribution upon which is superposed an electrostatic double-layer, producing no other effect than that represented by its electrical energy. Hence it need not happen that the maximum surface tension corresponds to zero potential difference, for the maximum surface tension may arise from the fact that non-electrical effects, accompanying the change in the potential difference and tending to reduce the surface tension, pass through a minimum value as the potential difference changes. This minimum value need not necessarily correspond to zero potential difference. The possible nature of non-electrical effects which may accompany changes in the potential difference is discussed later. The first part of the paper contains an experimental analysis of the Lippmann-Helmholtz theory.

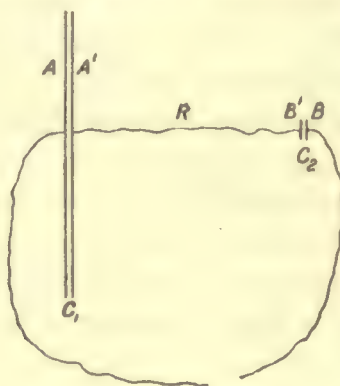
THE LIPPMANN-HELMHOLTZ THEORY OF ELECTROCAPILLARY PHENOMENA.

In the Lippmann-Helmholtz theory of the capillary electrometer there are in reality two distinct hypotheses, either of which may be separately justifiable. The first concerns the manner in which the potential difference at the capillary varies with the electromotive force applied between the terminals of the electrometer. The second deals with the relation between the above potential difference and the tension of the surface separating the mercury and the solution.

The First Hypothesis of the Lippmann-Helmholtz Theory.

The first hypothesis would apply to any electrolytic cell consisting of two polarizable electrodes placed in a conducting solution. When an E.M.F. (of which the value is kept within certain limits depending on the nature of the electrodes and of the solution) is applied to such a cell there may be a considerable current for a very short time; but the system almost at once assumes a practically steady state in which there is only a very feeble continuous current through the cell. The value of this current can in general be neglected in comparison with the current value found by dividing the E.M.F. applied by the calculable resistance of the electrolyte. It is therefore considered that the potential fall within the liquid can be neglected in comparison with the sum of the potential changes in the neighbourhood of the electrodes, and that this sum is equal in value to the applied E.M.F. The system is, in fact, considered equivalent to a pair of condensers (supposed existent at the surfaces of separation between electrode and solution) connected in series by a resistance (represented by the resistance of the electrolyte). For electrodes of the same nature in the same solution the respective capacities are taken to be proportional to the areas of the surfaces in contact with the solution. In the capillary electrometer, therefore, the capacity of one electrode would in general be indefinitely small compared with that of the other.

Let AA' and BB' represent condensers (of capacities C_1 and C_2) of which the plates



A' and B' are connected by a resistance R, and of which the "external" plates A and B are at first also connected.

Suppose the condensers are charged, and let A and B be at zero potential while A' and B' are at the potential $-\pi_n$. Let now an E.M.F. π_e be introduced in the external circuit connecting A and B, and let the resistance of this circuit be R' . Let π , π' and π'' be the final potentials of A, A' and B' respectively, — B being supposed kept at zero potential. Then it is easy to show that

$$\pi_e = \left(\frac{1}{c_1} + \frac{1}{c_2} \right) \int_0^{\pi} i dt,$$

in which the integral represents the quantity of electricity that has passed in the circuit during the time τ taken by the system to acquire its steady state. Also

$$\pi = \pi_e$$

$$\pi' = (\pi_e - \pi_n) - \frac{1}{c_1} \int_0^\tau i dt$$

and

$$\pi'' = \frac{1}{c_2} \int_0^\tau i dt - \pi_n = \pi'.$$

Now if the condenser AA' is very large compared with the condenser BB', we may neglect $\frac{1}{c_1}$ in comparison with $\frac{1}{c_2}$, so that we get

$$\pi'' = \pi_e - \pi_n$$

and

$$\pi - \pi' = \pi_n.$$

Thus the effect of introducing the E.M.F. π_e is that the potential difference at the small condenser is changed from $-\pi_n$ to $\pi_e - \pi_n$, while the change at the large condenser is negligible.

If the supposed analogy were complete, we should, therefore, have the result that in the capillary electrometer the variation of the potential difference at the capillary electrode is the same as the variation of the E.M.F. applied between the terminals. The analogy between the condenser system and the electrolytic cell cannot, however, be complete. In the latter case the original potential difference (corresponding to $-\pi_n$) is not arbitrary, but represents one of the conditions of the equilibrium at the electrode. Any cause which tends to alter the "natural" potential difference $-\pi_n$ at the small electrode—the nature of the solution in the neighbourhood of the electrode remaining sensibly constant—must in general be accompanied by a "depolarization" current representing the continual tendency of the "polarized" electrode to revert to the original potential difference. We cannot, therefore, have $i = 0$ in the final steady state as in the condenser system.

The Effect of Depolarization.

If we assume, however, that the effect of the depolarization is to produce a fall of potential within the electrolyte according to Ohm's law, the nature and magnitude of the effect can be readily specified. Thus, taking the symbols as above to be applicable to the capillary electrometer, we shall have

$$\pi_e - \pi = R' \cdot f(\pi'')$$

and

$$\pi' - \pi'' = R \cdot f(\pi''),$$

in which the continuous depolarization current is written as a function of π'' , because of the assumption that if the area of the capillary electrode is kept constant, the magnitude of the current will depend only on the potential fall at that electrode. It is not to be expected that the depolarization current will remain constant for an indefinite time. Owing to the variation of the concentration of the solution in the neighbourhood of the electrode, which must necessarily accompany the passage of the current through the electrolyte, the relation between π'' and the depolarization current will alter; but an effect of this kind will be gradual, and we may consider the depolarization current to be constant for some time after the introduction of π_e . In like manner, the accumulated effect of the continuous current upon the potential fall at the large electrode will only be gradually perceptible.

Adding the two above equations, and putting $\pi - \pi' = \pi_n$, we get

$$\pi'' + (R + R')f(\pi'') = \pi_e - \pi_n.$$

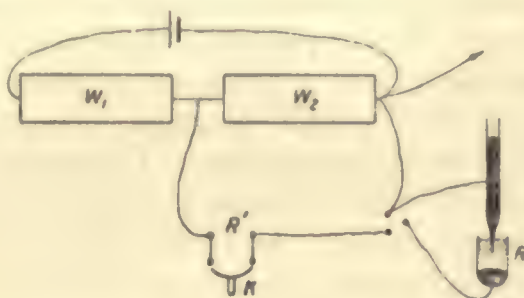
It therefore follows (as is otherwise obvious), that the effect of depolarization would be to cause the potential difference at the small electrode to change less rapidly than the applied E.M.F. Hence, before one can proceed beyond the first hypothesis to examine quantitatively whether the second hypothesis, concerning the relation between the potential difference and the surface tension, is true, it is necessary to determine whether the effect of the depolarization can under any circumstances become appreciable.

The magnitude of the effect will depend upon the value of $(R + R')f(\pi'')$. The internal resistance, R , will, of course, depend upon the nature of the electrolyte employed, upon the internal cross-section of the capillary tube and upon the distance between the mercury meniscus and the point of the capillary tube. Its value may range from something like 50,000 or 100,000 ohms to a million ohms or more. So that, under usual circumstances, the external resistance, R' , can be neglected in comparison with R . The value of $f(\pi'')$ will depend upon the area of the mercury meniscus. It will, therefore, be possible in a given electrometer to vary the value of $Rf(\pi'')$ for a given solution, and (by comparison of the curves for two different positions of the meniscus) to determine whether the form of the curve is appreciably affected by the change. On the other hand, the effect may be rendered directly evident and measurable by interposing a very high resistance in the external circuit, so that, although $f(\pi'')$, and even $Rf(\pi'')$, may be very small, $R'f(\pi'')$ will have an easily observable magnitude.

Experimental Determination of the Magnitude of the Depolarization Effect.

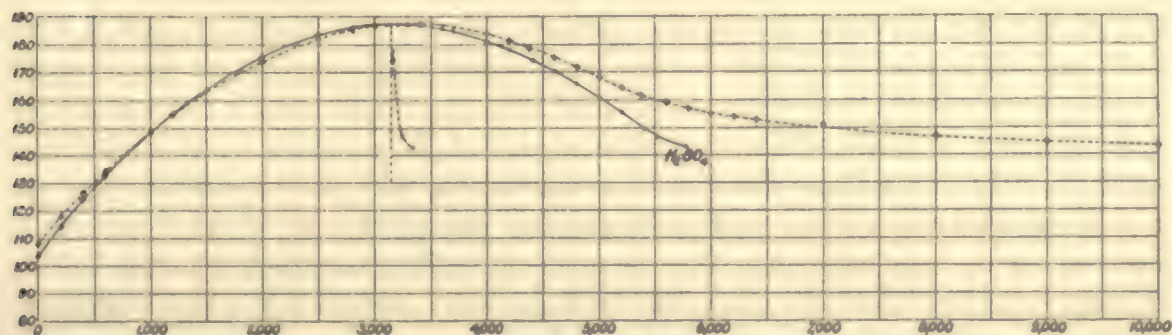
I have used this latter method, and the following experiments may be given in illustration of it. The high resistance consisted of graphite rulings upon ebonite, and

in the experiments in question had an approximate value of 10 megohms. The arrangement was as in the diagram :—



The graphite resistance could be cut out of the circuit by means of the key K. For each E.M.F. applied, the direct reading with R' cut out of the circuit (as in the ordinary method of determining capillary curves), was taken ; the "indirect" reading with R' in the circuit was then observed. The results for a solution of sulphuric acid are shown in fig. 1. The ordinates are the scale readings of the summit of the

Fig. 1.



mercury column of the electrometer, and the abscissæ denote the values of the resistances unplugged in the resistance box W_2 . 1000 ohms correspond approximately to 0.28 volt. These depolarization experiments were made in June, 1896, with an electrometer slightly different from that described later in the paper.*

* These experiments were described in a Dissertation presented at Trinity College, Cambridge, in August, 1896. I have since found that WIEDEBURG has also indicated, *theoretically*, the effect of depolarization. 'Wied. Ann.,' 59, 1896 (October). WIEDEBURG's conclusion concerning the *possible* magnitude of the depolarization effect is not supported by the experimental results contained in this paper. For example, when the surface tension has its maximum value at the capillary electrode in an electrometer containing a normal solution of potassium iodide, he suggests a possible potential fall of about 0.25 volt within the electrometer solution (due to a depolarization current) as a means of reconciling certain results, mentioned later, with the ordinary Lippmann-Helmholtz theory. The actually observed depolarization current for a KI solution is far smaller than that required to substantiate WIEDEBURG's suggestion, and, apart from this, the relations established later are at variance with his view.

The method of taking the electrometer curves and their degree of accuracy is discussed later.

The dotted curve represents the indirect curve, while the continuous one represents the ordinary capillary curve. In this particular experiment it apparently happened that for some accidental reason (such as difference in purity of the mercury of the large and small electrodes) the "natural" potential difference at the small electrode was appreciably different from that at the large. In consequence of this, the surface tension of the small electrode began to increase immediately the connection between it and the large electrode was broken. As I have subsequently observed, this is an effect which can be obviated when due care is taken, with pure mercury and a solution of uniform concentration. The phenomenon does not affect the conclusions in the present case, but in fact rather increases the interest attaching to the observations. When the electrodes were joined by a short wire, the surface tension was different from what it was when they were joined by the graphite resistance. The reading in the latter case was not appreciably affected by reversing the resistance, so it could be assumed that the graphite did not introduce any appreciable E.M.F. into the circuit.

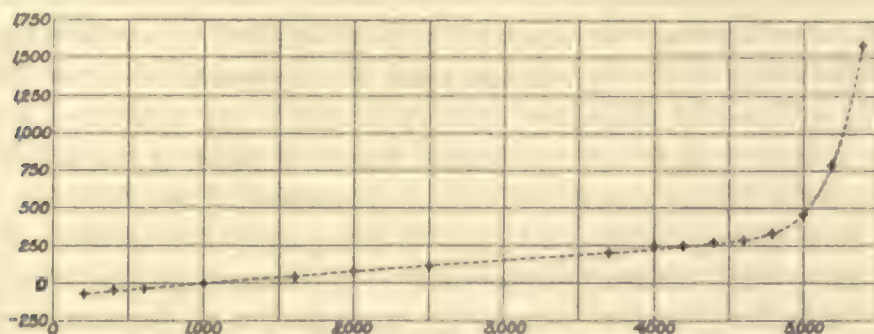
At first the indirect readings for a given external E.M.F. give higher values for the surface tension than the direct. The curves cut one another at an E.M.F. corresponding to about 0.28 volt, so that for this E.M.F., the surface tension assumed by the mercury is the same whether the E.M.F. is applied directly or through a very high resistance. Hence, when the surface tension at the capillary has this particular value, there can be no appreciable continuous current through the electrometer. It was found that the surface tension in question was practically identical with that assumed by the capillary, when the electrometer was disconnected from the rest of the apparatus—the electrodes being also unconnected. From this it is highly probable that this surface tension corresponded to the natural potential difference at the small electrode, and the significance of the disappearance of the depolarization current becomes immediately clear.

The horizontal distance between two points corresponding to the same surface tension, one on each curve, is a measure of the depolarization at the small electrode when the potential difference there has the value corresponding to the given surface tension. The actual value of the current is equal to the above horizontal distance (expressed in volts), divided by the value of the graphite resistance in ohms.

The curve in fig. 2 shows how the depolarization current varies with the externally applied E.M.F. The depolarization, apparently for a considerable range, is nearly proportional to the extent by which the potential difference at the small electrode has been displaced from its natural value. The ordinate of any point on this curve is the horizontal distance between a given point on the direct curve and the corresponding point on the indirect curve; the abscissa is the same as that of the given point on the direct curve. Since each of the curves has a maximum

ordinate, they cross one another a second time. In the neighbourhood of the maxima the horizontal distances between the curves are not very accurately determinable; but the general nature of the depolarization curve is obvious.

Fig. 2.



The vertical dotted line in fig. 1 is drawn as nearly as possible through the highest point of the capillary curve. Immediately to the right of this line there is a dotted curve. The points required to determine this curve were obtained by bisecting the horizontal lines drawn between points on the direct curve corresponding to the same surface tension. Considering any horizontal line, therefore, the intercept made on it between the vertical line and the above dotted curve represents the extent by which a point on the descending branch departs from symmetry with the corresponding point on the ascending branch, with respect to the vertical axis. The whole curve, therefore, represents the manner in which the descending branch of the capillary curve departs from symmetry with the ascending branch, with respect to a vertical axis through the point of maximum surface tension. The internal resistance of the electrometer used in the experiment above described was certainly less than 100,000 ohms, and probably not much above 50,000 ohms. Hence the depolarization effect upon the form of the curve, due to the internal resistance of the electrometer, lay between 0.5 per cent. and 1 per cent. of the corresponding effect due to the external resistance of 10,000,000 ohms. From an examination of the horizontal distance between the ascending branches of the direct and indirect curves we therefore see that the depolarization effect (due to the internal resistance) upon the ascending branch of the direct curve is negligible within the limits of observation.

The ascending branch of the curve can, therefore, be taken to be sensibly independent of the depolarization. It is seen from the indirect curve, however, that the depolarization current continues to increase after the maximum is passed, and that, eventually, the rate of increase becomes very rapid. It is also evident from the curves that the rate at which the descending branch of the direct curve departs from symmetry with the ascending branch is very similar to the rate at which the depolarization current increases. The departure from symmetry might, therefore, be very well due to the depolarization.

In order to determine whether the depolarization is the sole cause of the observed flattening of the direct curve, an accurate knowledge of the relation between the graphite resistance and the internal resistance of the electrometer would be necessary. But an approximate knowledge of this relation is quite sufficient to show that the depolarization must soon affect the form of the curve. Thus, to take an example, the horizontal distance between the direct and indirect descending branches for a surface tension corresponding to 150 is not less than 64 horizontal divisions (see fig. 1), equivalent to a potential difference of 1600 ($= 1.6 \times .28$ volt), and even if the electrometer resistance is not above 50,000 ohms, the effect of the latter will be a displacement of the direct curve to the right to the extent of one-third of a horizontal division—a quite perceptible amount—due to the potential fall within the electrometer. As the actually observed displacement is considerably greater than the above, it seems probable that the flattening in the upper portion of the curve is not due to depolarization alone. This is rendered still more probable when the curve for such a substance as hydrochloric acid (in which the ascending branch is very much steeper than the descending) is considered.

Fig. 3.

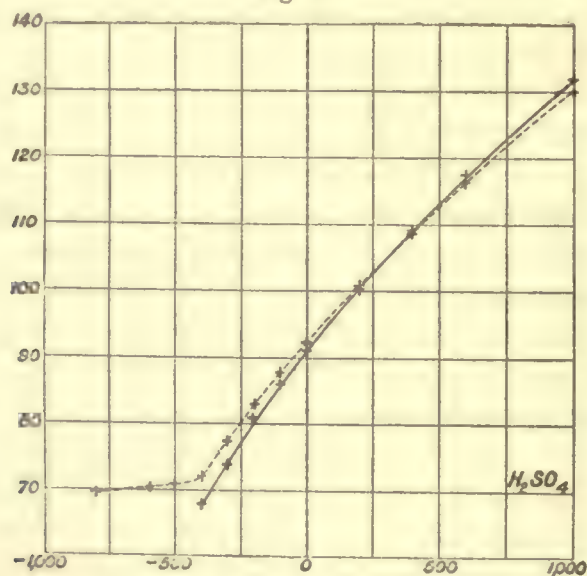


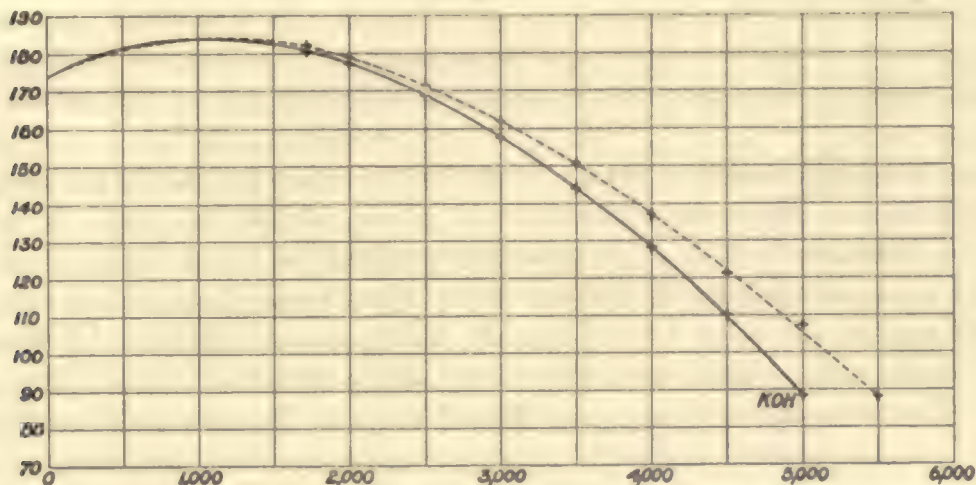
Fig. 3 gives a portion of another pair of direct and indirect curves, showing how the depolarization increases when the potential difference applied between the terminals of the electrometer is reversed in sign.

In order to show how the depolarization for cathodic polarization of the small electrode varies with the nature of the kation, curves (corresponding to those above described) are given for a dilute solution of caustic potash (fig. 4).

The curves show that in this case, for a given surface tension, the depolarization is very much less than when the kation is hydrogen of the same order of concentration. As is well known, the magnitude of the depolarization in an electrolytic cell depends

not only upon the chemical nature of the ions, but also upon their concentration in the solution. This can be readily rendered obvious by the above method.

Fig. 4.



For the above solution of potash it is clear that within the range of the experiment the effect of depolarization upon the direct curve can be considered negligible. The same can be said of most of the solutions considered later.

The Second Hypothesis of the Lippmann-Helmholtz Theory.

The second hypothesis in the Helmholtz explanation of electro-capillary curves is that the electrical effect upon the surface tension is a purely electrostatic effect depending at a given potential difference upon the capacity of the electrode per unit area. It supposes that, in general, the capacity per unit area is independent of the chemical nature of the solution employed in the electrometer. From the approximately parabolic nature of some of the curves through a considerable portion of their course, the Helmholtz theory leads not only to the view that through the range considered the capacity per unit area is constant, but also makes it possible for the value of this capacity to be calculated. Assuming the inductive capacity of the dielectric of the double layer to be unity, the theory further allows an estimate to be formed of the distance between the parallel charges forming the double layer. That the distance so calculated is of the same order of magnitude as molecular distances calculated in other ways is, however, no proof of the validity of the Helmholtz view. For the distance between the layers, as so calculated, might have amounted to something very much larger without standing in opposition to other known data concerning molecular distances. In other words, there is no *a priori* objection to a view which supposes that the capacity per unit area of the common surface may really be much

smaller than the Helmholtz view requires.* If such a view as this were true, the electrostatic effect would be insufficient to account for the observed variation in the surface tension. Assuming the potential difference, the existence of the electrostatic effect is scarcely open to doubt, it is only the relative importance of the effect that may be questioned. The electrostatic effect apart, the Helmholtz view assumes that the nature of the transition from the solution to the mercury is (through a considerable range) independent of the potential difference and of the nature of the solution.

Several published observations show that there are cases for which this assumption cannot be true. There are many facts in favour of the view that for a given potential difference there is a corresponding condition (of the partly physical, partly chemical kind, pictured by WARBURG) of the space bounded on the one side by the mercury, and on the other by the sensibly homogeneous solution. Obviously the surface tension will depend upon the nature of the transition through the surface layer. The mode of transition may depend only on the chemical nature of the solution and the potential difference across the space in which the transition takes place. On this view the electrostatic effect and the mode of transition for a given solution will be determined by the potential difference, and therefore the surface tension will be fixed by the potential difference. It remains to determine how the relation between the surface tension and the potential difference depends upon the chemical nature and concentration of the solution.

It is scarcely necessary now to set forth the arguments against the second hypothesis of the Helmholtz theory of the electrometer; but I shall endeavour to show by consideration of observations of the type held to throw greatest doubt upon the theory, that the first hypothesis gives results in close accord with the facts, and need not therefore be abandoned, even if the second should be proved untenable.

RELATION BETWEEN THE LIPPMANN-HELMHOLTZ THEORY AND OTHER THEORIES OF ELECTROCAPILLARY PHENOMENA.

It may be well to point out the relation such results bear to the theory of WARBURG, which is, perhaps, the most strongly advocated in opposition to the Helmholtz theory. Strictly speaking, the Warburg theory deals only with the ascending branch of the curve. It ascribes the increase in surface tension to the diminution in the concentration of a mercury salt in the neighbourhood of the capillary meniscus. According to WARBURG the effect of an E.M.F. established between the terminals of the electrometer is to convert the latter into a kind of concentration cell. Part of the E.M.F. of this cell will presumably be due to a potential difference within the electrolyte. The conclusions drawn later depend upon observations of the descending portions of capillary curves, which are usually much

* Cf. WARBURG, 'Wied. Ann.,' 1890, vol 41.

more definite and more accurately measurable than the ascending portions ; but unless the concentration E.M.F. within the electrolyte is supposed to be the same for quite different liquids subjected to very different degrees of polarization, there does not seem to be any simple method of reconciling the results with the Warburg theory. G. MEYER* has attempted to complete WARBURG's theory of the phenomena by supposing that the descending portions of the curves are produced by formation of an amalgam between the mercury and the element forming the kation of the solution, while LUGGIN† has endeavoured to show that the descending branch of the curve is absent when the solution does not contain hydrogen. The experimental evidence adduced in favour of these views is mainly qualitative in nature. An extended examination of the quantitative relation between the capillary curves for differently concentrated solutions of the same salt shows that difficulties arise in the quantitative application of the idea that the surface tension in the descending branch depends only upon the concentration of the amalgam upon the electrode surface.

While it is unnecessary to deal with the nature of these difficulties at present, since they do not immediately concern the experiments first discussed, it may be pointed out that if the first hypothesis of the Helmholtz theory be true, it is possible to trace (by means of the capillary curves) the relation between the variation of the potential difference at the capillary electrode, the surface tension and the nature and concentration of the electrolyte. Probably it is only by the investigation of the relation between these quantities that the value of the capillary curves, as a method of determining "single potential differences" in voltaic phenomena, can be definitely fixed.

THE DISCREPANCY BETWEEN THE LIPPMANN-HELMHOLTZ THEORY AND THE NERNST-PLANCK THEORY OF THE POTENTIAL DIFFERENCE BETWEEN SOLUTIONS.

The result, derived from the Helmholtz theory, that the E.M.F. which must be applied between the terminals of the electrometer to cause the capillary electrode to assume its maximum surface tension, is equal to the natural potential difference between the large electrode and the solution, is so important, if true, that this E.M.F. has been observed for a large number of solutions. It is, however, impossible to test directly the validity of the numbers so found, since no other independent means of determining single potential differences has, up to the present, been discovered —if we except the dropping electrode method (which will be referred to later).

We may set up and measure the E.M.F. of a cell of the type



* MEYER, 'Wied. Ann.,' 45, 1892.

† LUGGIN, 'Zeits. f. Physik. Chemie.,' 16, 1896.

where M_1X_1 and M_2X_2 signify two solutions which have been examined in the capillary electrometer; but the E.M.F. found cannot be applied to test the Helmholtz theory of the electrometer unless we know the value of the potential difference between the two solutions.

The state of our knowledge of the potential differences between liquids is not satisfactory. Within recent years, however, NERNST,* starting from the dissociation hypothesis, has given a theoretical investigation for the case in which the two liquids are solutions of the same salt, but of unequal concentration. PLANCK† has extended the investigation to the case in which the liquids are solutions of different salts. In many cases the values found experimentally agree very closely with those calculated; but it must be borne in mind that in the experiments the potential difference between the liquids only formed part of the E.M.F. actually measured. For example, in testing the formula as applied to two solutions of potassium chloride of different concentrations, it is necessary to introduce a fresh hypothesis in order to calculate the difference between the potential difference between mercury, covered with calomel, and the stronger solution, and the potential difference between mercury, covered with calomel, and the weaker solution.‡ In order to show the nature of the agreement between the calculated values and those found experimentally, some results for KCl solutions are given below. In the first column are given the concentrations in gram equivalents per litre; in the second the observed E.M.F.s of cells of the type;



and in the third the calculated values of these E.M.F.s.

Concentrations. Gram equivalents per litre.	Observed E.M.F.	Calculated E.M.F.
	volts.	volts.
3.0 and 0.5	.0443	.0402
1.0 „ 0.1	.0533	.0525
0.5 „ 0.1	.0359	.0367
0.1 „ 0.05	.0162	.0162
0.1 „ 0.02	.0387	.0380
0.1 „ 0.01	.0545	.0548
0.05 „ 0.01	.0387	.0384

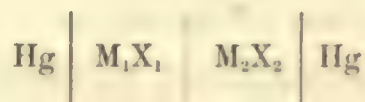
These observations form part of a series of experiments which will be described later.

* NERNST, 'Zeits. f. Physik. Chemie,' 4, 1889.

† PLANCK, 'Wied. Ann.,' 39, 1890, and 40, 1890; cf. also NEGBAUR, 'Wied. Ann.,' 44, 1891.

‡ NERNST, 'Zeits. f. Physik. Chemie,' 4, 1889.

In a cell of the type



let π_{n_1} and π_{n_2} be the respective potential differences between mercury and the solutions (calculated on the Helmholtz theory of the capillary electrometer), and let π_{12} be the potential difference between the liquids and π_e the observed E.M.F. of the cell, then we should have

$$\pi_e = \pi_{n_1} - \pi_{n_2} + \pi_{12}.$$

ROTHMUND has made observations upon cells of this type and has found values for π_e , π_{n_1} and π_{n_2} for a number of different solutions. The following table gives the results of some of his experiments:—

M_1X_1	M_2X_2	π_e	π_{n_1}	π_{n_2}	$\pi_e - (\pi_{n_1} - \pi_{n_2})$
nKCl	nKI	·349	·560	·437	·226
nKCl	nKCNS	·172	·560	·534	·146
nNa ₂ S	nKCl	1·006	·560	— ·030	·416

He estimates the possible error in the determination of π_{n_1} and π_{n_2} from the curves to be not greater than 0·01 volt.*

Referring to such experiments, NERNST says:—"While, therefore, the Helmholtz hypothesis concerning electrocapillarity is found to be in good agreement with the osmotic theory . . . as far as the qualitative side of the phenomena goes, we come upon serious contradictions so soon as we proceed to a quantitative comparison. As results of the electrocapillary method of measuring contact potentials, we obtain the following table:—

HCl H ₂ SO ₄	·025	·010
KCl HCl	·022	·028
KCl KCNS	·161	·000
KCl KI	·247	·000
KCl Na ₂ S	·419	·000

Column 1 gives the symbols of the solutions examined; column 2 contains the values of the potential differences between them deduced from the Helmholtz theory of the electrometer; and column 3 gives the values of the same potential differences calculated according to the osmotic theory. The differences are great, and not explicable as errors of observation.†

* ROTHMUND, 'Zeits. f. Physik. Chemie,' 15.

† NERNST, 'Wied. Ann.,' 58, Beilage, 1896.

SOLUTIONS OF POTASSIUM CHLORIDE AND POTASSIUM IODIDE.

1. *The Potential Difference between Equally-concentrated Solutions.*

The experiments show that the Helmholtz theory of the electrometer and the Nernst-Planck calculations of the potential differences between solutions cannot both be true. While there are many facts in favour of the view that the Nernst-Planck hypothesis gives the quantitative expression for the potential difference between two solutions, there is one result calculated from the hypothesis which seems to possess greater weight than any of the others, since it would seem to be a consequence of almost any form of diffusion hypothesis. This is the result that the potential difference between equally-concentrated solutions of potassium chloride and potassium iodide is so small that in measurements of the type with which we are concerned it can be taken to be zero.

KOHLRAUSCH has investigated the electrolytic conductivity of solutions of KCl and KI for different degrees of dilution, and an examination of his numbers shows the relative amount of ionization in equally-concentrated solutions of the two salts may be considered identical when the solutions do not contain more than 0.01 gramme molecule per litre ($\frac{1}{100}$ th normal). Even when the strengths correspond to a gramme molecule in 2 litres ($\frac{1}{2}$ normal) the coefficients of ionization only differ by about two per cent.* Again, according to the most recent values, the ionic velocities of chlorine and iodine are practically identical.† When, therefore, dilute solutions of KCl and KI of equal strength are brought into contact there can be no tendency of the potassium ions to diffuse, while the chlorine and iodine ions will tend to diffuse with equal velocities across the common surface. Granting the ionic hypothesis we may, therefore, safely assume that no forces which tend to alter the quantity of electricity in the unit of volume act across the surface of separation between the liquids, and that, therefore, no potential difference will arise between the liquids.

2. *The Nature of the Electrocapillary Curves for the same Solutions.*

For the reason given above I have carefully examined the relation between the capillary curves for KCl and KI in order to determine further the result of the hypothesis that the potential difference between equally-concentrated solutions of KCl and KI is zero.

(a.) *General character of electrocapillary curves.*

The behaviour of the meniscus in the capillary electrometer is in general very different in the "ascending" portion of the curve from what it is in the "descending"

* KOHLRAUSCH, 'Wied. Ann.,' vol. 26, 1885.

† KOHLRAUSCH, 'Wied. Ann.,' vol. 50, 1893.

portion. In the ascending portion the mercury is often apparently sluggish, and the surface tension becomes difficult to measure. Further, the surface tension may take up a certain value immediately after a given potential difference is established between the terminals of the electrometer, and then fall gradually as the time of contact continues. In contrast with this, the surface tension in the descending portion of the curve is almost always very definite. Moreover, while the form of the ascending portion is widely different for solutions with chemically different anions, and even noticeably different for unequally concentrated solutions of the same salt, the form of the descending portion, for a considerable part of its course, is the same (within the limits of experimental error) for equally-concentrated solutions of quite different salts, and only varies very slightly for unequally concentrated solutions of a given salt.

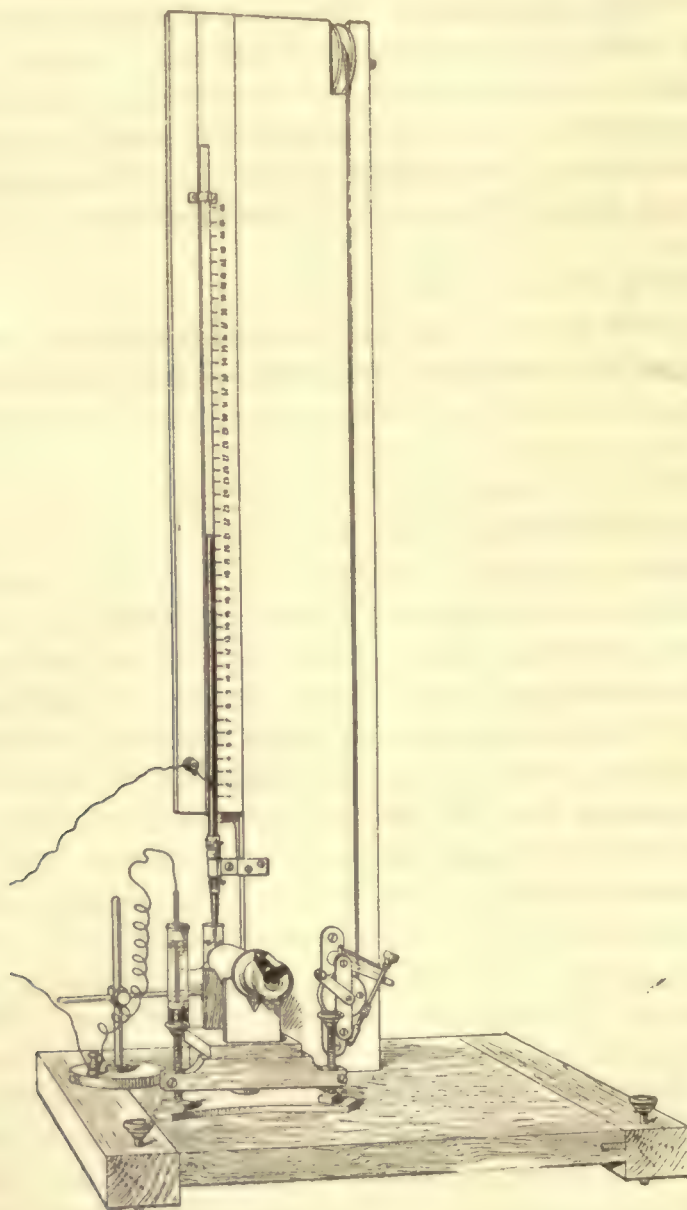
(b.) *Definite nature of the descending branches.*

While therefore both the ascending and descending branches have been observed, the first conclusions are based upon observation of the descending portions of the curves. These were definite and amenable to quantitative treatment.

(c.) *Method adopted in examining the electrocapillary curves, and discussion of the degree of accuracy attainable in the experiments.*

The form of electrometer that I have used has a movable mercury reservoir in direct communication with the mercury column supported by the surface-tension effect at the capillary electrode. The mercury reservoir can be raised or lowered by means of a flexible cord, wound upon a bobbin, having a tangent-screw fine adjustment. By means of this arrangement the small electrode can be maintained at a constant position in the capillary tube. The diameter of the capillary—the same one was used in determining the curves for a large number of solutions—was about 0.003 centim., and the usual length of the column of solution between the meniscus and the point of the capillary was 0.057 centim. The resistance of such a column (supposed cylindrical) would, if the solution were normal KCl at 18°, be approximately 83,000 ohms. The position of the capillary meniscus was fixed by means of a scale within the microscope. The apparent magnitude of a division of this scale is about 1.5 millim. Every tenth division of the scale is marked. When the position of the microscope is so adjusted that the zero of the micrometer scale coincides with the end of the capillary, the fortieth division (marked 4) of the scale is practically in the centre of the field. The meniscus was always made to coincide as nearly as possible with the central division of the scale. The height of the mercury column, supported by the capillary electrode, when possessing its maximum surface tension in such a solution as dilute sulphuric acid, was about 440 millims. The variation of the surface tension was observed by means of a scale divided into millimetres placed directly behind the mercury column. The greatest error in the scale division was about 1 part in 500. The conclusions first drawn from the curves are practically

independent of the accuracy of the division of the scale. The zero of this scale was about 12.4 centims. above the capillary point, so that the reading corresponding to the maximum surface tension, in dilute sulphuric acid, was about 31.6 centims. The position of the summit of the mercury column relative to the scale could be deter-



mined to within about a tenth of a millimetre. It would not be difficult to arrange for a greater degree of accuracy in this measurement; but, apart from the increase in the time occupied by the observations, which more delicate determination would involve, the above error does not exceed that introduced from other causes. Usually the solution to be examined was placed in a Clark cell tube of the Rayleigh H form.

The mercury forming the large electrode was placed at the bottom of one limb; the capillary electrode dipped into the other limb. In order that the definition of the capillary meniscus might be as good as possible, the capillary was placed close to the side of the limb that received it. After the curve for the solution had been determined, the H tube, containing it, was removed and replaced by another containing a different solution. It would have been very inconvenient to have worked always with the same H tube, as in many cases it was desirable to allow the solution to stand some considerable time over mercury before examining it in the electrometer. A number of H tubes were used, and naturally these were not precisely similar. In every case the definition of the capillary meniscus, when at the fortieth division of the scale, was made as good as possible; but it did not always happen that the definition of the capillary point was then correspondingly good. However, the maximum error in the setting of the capillary point was not greater than about one of the small scale divisions, while it could usually be set at the zero within two-tenths of a small scale division. The capillary meniscus could be readily set at the fortieth division with an error of less than one-tenth. An error of a scale division in the setting of the meniscus produced a maximum error of about .4 millim. in the reading of the summit of the mercury column. Under ordinary circumstances, therefore, the error introduced into the surface tension observations by the necessary replacement of one H tube by another was not greater than .08 millim.

In order to remove one solution from the interior of the capillary tube before the introduction of the succeeding one, the following method of procedure was adopted. The capillary tube was immersed in a beaker of distilled water, and by alternately lowering and raising the mercury reservoir, the water could be drawn into the tube and then again expelled along with a little mercury. This process was repeated several times, the excursions of the meniscus in each case being very much longer than any that occurred during the experiments, as the result of electrical effects. The beaker was then withdrawn, and as much of the water as possible was removed from the capillary. A similar process was then adopted in order to fill the capillary with the solution next to be examined. To test the sufficiency of this treatment, a second set of observations upon a given liquid was made, several other solutions having been used in the electrometer during the interval. The first and second sets were found to agree within the limits of experimental error. In a case where one solution was followed by a more concentrated one of the same salt, the intermediate operation with distilled water was, of course, unnecessary.

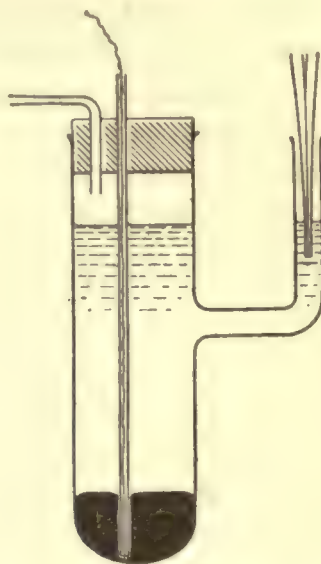
The potential difference between the terminals of the electrometer was varied by means of an ordinary potentiometer arrangement. The potentiometer circuit consisted usually of a secondary cell (E.M.F. about 2.03 volts) and two resistance boxes in series. The sum of the resistances introduced into the circuit by these boxes always amounted to 10,000 ohms. Usually the resistance in each box was altered by 500 ohms at a time, so that the corresponding change in the potential difference

applied between the electrometer terminals was about a tenth of a volt. The probable error of each of the box resistances was less than a tenth per cent., and the constancy of the potentiometer current was tested by means of a standard Clark cell, of which the E.M.F. at 15° was known to be within one-tenth per cent. of 1.434 volts. The accuracy of the potential measurement was therefore considerably greater than that which could be conveniently given to the surface tension observations.

(d.) *The Electrocapillary Curves for KCl and KI.*

1. *Preliminary Experiment.*—Before proceeding to the experiments of the ordinary capillary electrometer type, mention may be made of a simple means by which very suggestive results as to the relation between capillary curves may be obtained.

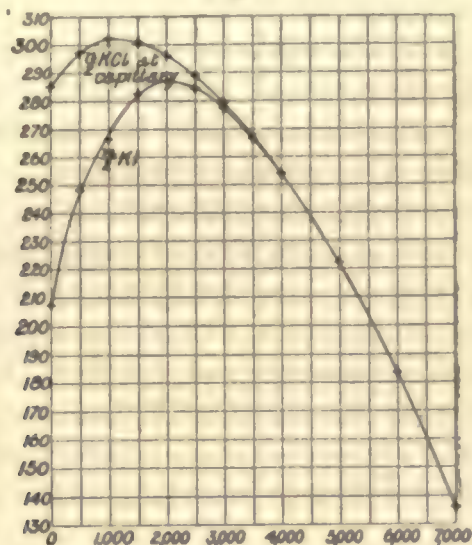
A vessel for containing the solution is constructed of the shape shown in the figure.



The mercury forming the large electrode is placed at the bottom of the main tube. The point of the capillary is brought within the smaller tube. The vessel is first filled with a solution of one of the salts (say $\frac{1}{2}n$ KI), and the capillary curve is determined. Withdrawing air from the apparatus by means of the side tube at the top of the main tube, the liquid rises in the latter and falls in the narrow tube. After the small tube has been nearly emptied, it is filled to the level of the liquid in the main tube with a solution of the other salt (say $\frac{1}{2}n$ KCl), and the capillary curve is again taken.

Fig. 5 shows the forms of the resulting curves for the solutions in question. The numbers from which the curves were constructed are as follow :—

Fig. 5.



Applied E.M.F.	$\frac{1}{2}n$ KI.	$\frac{1}{2}n$ KI with capillary in $\frac{1}{2}n$ KCl.
0	20.75	28.51
500	24.9	29.75
1000	26.69	30.23
1500	28.3	30.1
2000	28.71	29.69
2500	28.47	28.88
3000	27.73	27.88
3500	26.65	26.7
4000	25.39	25.38
5000	22.2	22.2
6000	18.3	18.3
7000	13.52	13.55

The surface tensions in the ascending branches of the curves were somewhat uncertain and difficult to measure. The descending branches, however, were quite definite. It is seen that when the E.M.F. exceeded a value corresponding to the abscissa 4000 (= about .8 volt) the curves were identical. This result can be very readily explained on the double layer view of polarization in an electrolytic cell considered at the beginning of the paper, if we assume that the potential difference between $\frac{1}{2}n$ KI and $\frac{1}{2}n$ KCl can be neglected, and that there is no appreciable concentration E.M.F. within the liquid. Since the potential difference at the large electrode has not been altered between the two sets of experiments, the potential difference ($\pi_c - \pi_a$) at the small electrode for a given applied E.M.F. will be the same for both curves. When the applied E.M.F. is less than .8 volt., the surface tension does not depend merely upon the potential difference at the small electrode, but also upon the chemical nature of the solution. Now the solutions are the same in every respect

except that the anion in one is iodine, and in the other chlorine. Until the potential difference reckoned from the solution to the electrode reaches a certain value the effect of the anion upon the surface tension (*i.e.*, in determining the mode of transition from the solution to the mercury) is appreciable; but this effect gradually diminishes and finally disappears, as is shown by the fact that the form of the curve (beyond 4000) is independent of the nature of the anion.

From this point of view it is obviously futile to consider that the highest point of the iodide curve corresponds of necessity to zero potential difference between the KI solution and the mercury electrode, since it might equally well be argued that the highest point of the curve obtained with KCl at the capillary corresponded to zero potential difference between the mercury and the KCl. If there is no appreciable potential difference between the KI and the KCl both results cannot be true. The potential differences in the two cases (maximum surface tension) must differ by about 0.2 volt, or else the potential difference between $\frac{1}{2}n$ KI and $\frac{1}{2}n$ KCl must be about 0.2 volt.

In the face of evidence that there is a chemical effect of the anion upon the surface tension, and that this effect increases as the potential of the liquid with respect to the electrode decreases, it does not seem advisable to say more than that the potential difference (reckoned from the solution to the electrode) is considerably less at the maximum surface tension when the solution is KCl than when it is KI. The marked depression of the maximum value of the surface tension observable in the case of potassium iodide solutions is one of the characteristic features of the curves dealt with by ROTHMUND—the actual fact of the depression was apparently first noticed by GOUY,* but the depression is really a perfectly general phenomenon. The amount of depression depends upon the concentration of the solution as well as upon its chemical nature. The depression for concentrated solutions of chlorides is very pronounced, and for dilute solutions it can readily be observed that the maximum value of the surface tension rises as the concentration diminishes. It is obviously an effect which does not depend upon the density of the solution. For example, a saturated solution of caustic potash (which is soluble in about half its weight of water) has as high a maximum surface tension as a half-normal solution of potassium chloride. The effect of the ions (apart from the electrostatic effect) upon the surface tension would appear to depend, for a given potential difference, upon their nature and concentration in the solution. Whether the surface tension in the neighbourhood of the maximum is ever controlled by the electrostatic effect alone, depends (on this view) upon whether, when the potential difference between the solution and the electrode is small, the nature and concentration of the ions is such that their non-electrical effect upon the surface tension can be neglected.

In the case above considered the curves are identical when the applied E.M.F. exceeds 0.8 volt. The subsequent variation of the surface tension is therefore

* 'Comptes Rendus,' vol. 114, 1892.

presumably independent of the nature of the anion ; but it is obvious that we obtain no information from the curves as to whether their subsequent course is free from any non-electrostatic influence depending upon the kation. For the kation is the same and of the same concentration in the two solutions. It is, however, easy to extend the above observations so as to show that (granting the Nernst calculation gives at least approximately the potential difference between unequally concentrated solutions of the same salt), although the *form* of the lower portion of the descending curve varies very little with the strength of the solution, yet the surface tension for a given potential difference depends upon the strength of the solution. From this it would appear that the surface tension does not depend upon the electrostatic effect alone even when the anion effect has presumably disappeared ; but that, in fact, there is also a kation effect which becomes evident as the solution becomes increasingly positive with regard to the electrode.

2. *Final experiments showing the agreement of the first hypothesis of the Lippmann-Helmholtz theory with the Nernst-Planck theory of the potential difference between KCl and KI.*—We may, however, first apply to the ordinary electro-capillary curves for equally concentrated solutions of KI and KCl, the result suggested by the curves already given, that ultimately the descending branch of either curve is practically unaffected by the nature of the anion, and that if it is then influenced by the kation, the nature of the influence is such that, in equally concentrated solutions of salts possessing the same kation, the potential difference for a given surface tension is the same in both solutions. It is found that the descending branches eventually approximate very closely to parallelism. Considering the parallel portions, let π_c be the E.M.F. required to be applied between the terminals to produce a given surface tension for the KCl solution, and let π'_c be the E.M.F. required to produce the same surface tension for the KI solution. Then $\pi_c - \pi'_c$ is very approximately constant. Let $-\pi_n$ be the natural potential difference between the KCl solution and mercury (the electrode being considered positive to the solution), and let $-\pi'_n$ be the corresponding quantity for the KI solution. Then on the first hypothesis of the ordinary electrometer theory (applicable to any electrolytic cell), the potential differences between the solution and the capillary for the two points of equal surface tension (one on each curve) are

$$\pi_c - \pi_n \quad \text{and} \quad \pi'_c - \pi'_n$$

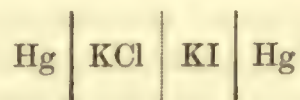
respectively. Now if we suppose the potential difference is the same in the two cases because the surface tension is the same, we get

$$\pi_c - \pi_n = \pi'_c - \pi'_n$$

or

$$\pi_n - \pi'_n = \pi_c - \pi'_c = \alpha,$$

where α , an observable quantity, is represented by the horizontal distance between the parallel portions of the curves. Let now a cell be constructed of the form



and let its observed E.M.F. be b , and suppose π_i is the potential fall from the KCl to the KI solution. Then

$$\pi_n - \pi_n' + \pi_i = b.$$

If $\pi_i = 0$, we must have

$$a = b.$$

The following experiments show the observed relation between a and b .

E.M.F. applied to electrometer [1000 = .202 volt].	Surface tension readings.		Horizontal distance between parallel por- tions of curves. (a.)	Calculated E.M.F. of cell Hg KCl KI Hg assuming P.D. between KCl and KI negligible.	Observed E.M.F. of cell Hg KCl KI Hg. (b.)
	$\frac{n}{2}$ KCl.	$\frac{n}{2}$ KI.		volt.	
0	23.5	20.39	1975 ± 6		
500	26.0	24.8			
1000	28.0	27.1			
1500	29.21	28.29			
2000	30.0	28.71			
2500	30.49	28.5			
3000	30.6	27.81			
3500	30.29	26.78			
4000	29.69	25.48			
4500	28.90	24.0			
5000	27.9	22.35			
5500	26.75	20.51			
6000	25.41	18.55			
6500	23.95				
7000	22.29				
				Calculated E.M.F. on ordinary Helm- holtz theory, assuming P.D. be- tween KCl and KI to be zero.	
				.162 volt (approx.)	
					1950 (max.) = .3940 volt.

E.M.F. applied to electrometer [1000 = .2027 volt].	Surface tension readings.		Horizontal distance between parallel por- tions of curves. (a.)	Calculated E.M.F. of cell Hg KCl KI Hg assuming P.D. between KCl and KI to be negligible.	Observed E.M.F. of cell Hg KCl KI Hg. (b.)
	$\frac{n}{10}$ KCl.	$\frac{n}{10}$ KI.		volt.	
0	24.78	19.9†	1725 ± 6		
500	27.40	25.6			
1000	29.0	28.34			
1500	30.2	29.73			
2000	30.65†	30.3			
2500	31.33	30.2			
3000	31.41	29.57			1729 ± .5
3500	31.2	28.6			=
4000	30.7	27.49		.3496	.3503 volt.
4500	29.99	26.13		± .0012	
5000	29.1	24.65			
5500	28.0	22.99			
6000	26.72	21.11			
6500	25.33	19.13			
7000	23.79	16.9			
7500	22.0	14.43			
8000	20.01	11.73			
8500	17.9				
9000	15.6				
E.M.F. for maximum surface tension				Calculated E.M.F. of cell assuming P.D. between KI and KCl zero, on ordinary Helm- holtz theory	
	$\frac{n}{10}$ KCl.	$\frac{n}{10}$ KI.			
	2800 ± 50	2200 ± 50		.122 (approx.)	

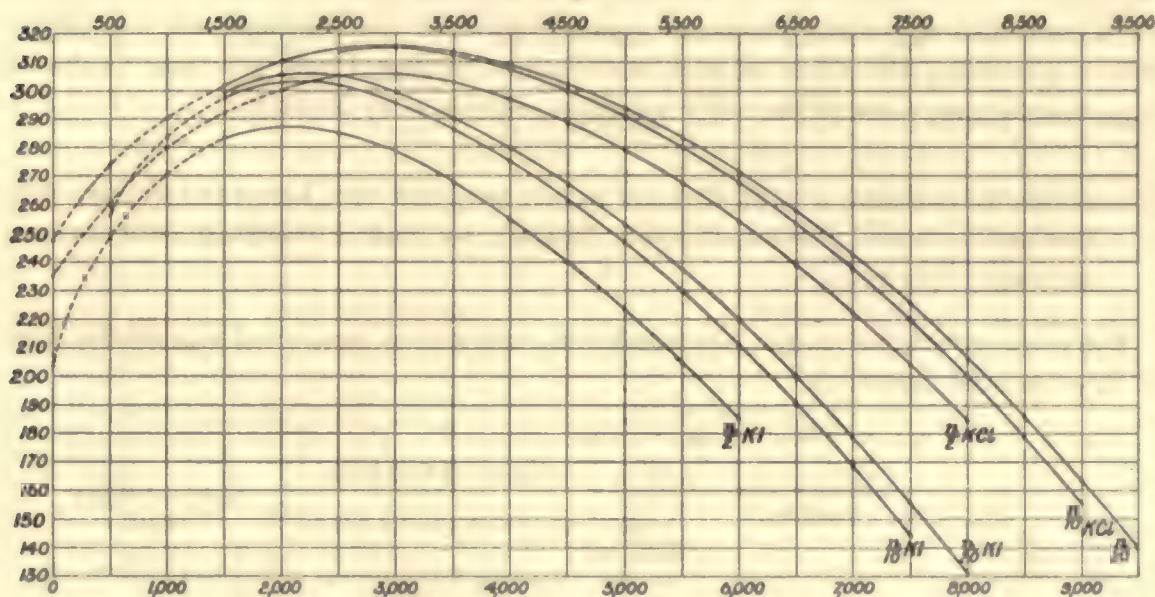
E.M.F. applied to electrometer [1000 = 2027 volt].	Surface tension readings.		Horizontal distance between parallel por- tions of curves. (a.)	Calculated E.M.F. of cell Hg KCl KI Hg assuming P.D. between KI and KCl zero.	Observed E.M.F. of cell Hg KCl KI Hg. (b.)
	$\frac{n}{20}$ KCl.	$\frac{n}{20}$ KI.		volt.	
0	25.1 ?	19.95 ?	1663 \pm 6		
500	27.4 ?	25.3			
1000	29.0 ?	28.35			
1500	30.18	29.92			
2000	30.99	30.57			
2500	31.45	30.49			1668 \pm 0.5
3000	31.5	29.9			=
3500	31.3	29.0			
4000	30.85	27.98		.3371	.3381 volt.
4500	30.2	26.72		\pm .0012	
5000	29.38	25.31			
5500	28.32	23.78			
6000	27.13	22.0			
6500	25.79	20.0			
7000	24.28	17.9			
7500	22.6	15.6			
8000	20.7	13.1			
8500	18.62				
9000	16.4				
9500	14.0				
	E.M.F. correspond- ing to maximum surface tension.			Calculated E.M.F. on ordinary Helm- holtz theory, assuming P.D. be- tween KCl and KI negligible.	
	$\frac{n}{20}$ KCl.	$\frac{n}{20}$ KI.			
	2950 \pm 50	2150 \pm 50		.162 (approx.)	

The corresponding curves are shown in fig. 6. In order to find a , the horizontal distances were measured directly from the curves, as it was more convenient to do this than to observe the difference between the E.M.F.s required to produce the same surface tension in the different solutions. The E.M.F. of the cell was determined immediately after the corresponding curves had been observed. The same potentiometer circuit was used in the determination of the curves and of the cell E.M.F. The constancy of this circuit was checked by means of a standard cell.

The curves for the half normal solutions are not strictly comparable with the others; they were taken (with the same electrometer) about a year before the latter, under slightly different conditions. Although in the case of the later KCl solutions the mercury was covered with a layer of calomel, it was not necessary to add a

“depolariser.”* When any one of the above solutions has stood for several hours over mercury, the electro-capillary curve determined from it can be treated as independent of the time, since it remains constant for a much longer period than a complete set of observations occupies. The E.M.F. of the $\text{Hg} \mid \text{KCl} \mid \text{KI} \mid \text{Hg}$ cell was determined by fixing the pair of H cells at a suitable distance apart, and adjusting so that the

Fig. 6.



solutions in the cells were at the same level. The tubes were then joined across by a capillary siphon (about 1 sq. millim. in cross-section) of which the total length was about 60 centims. Contact within the cell was made by carefully drawing the solutions to the centre of the siphon. Care was further taken to avoid any considerable shaking of the mercury surfaces. The diagram following represents the cell.



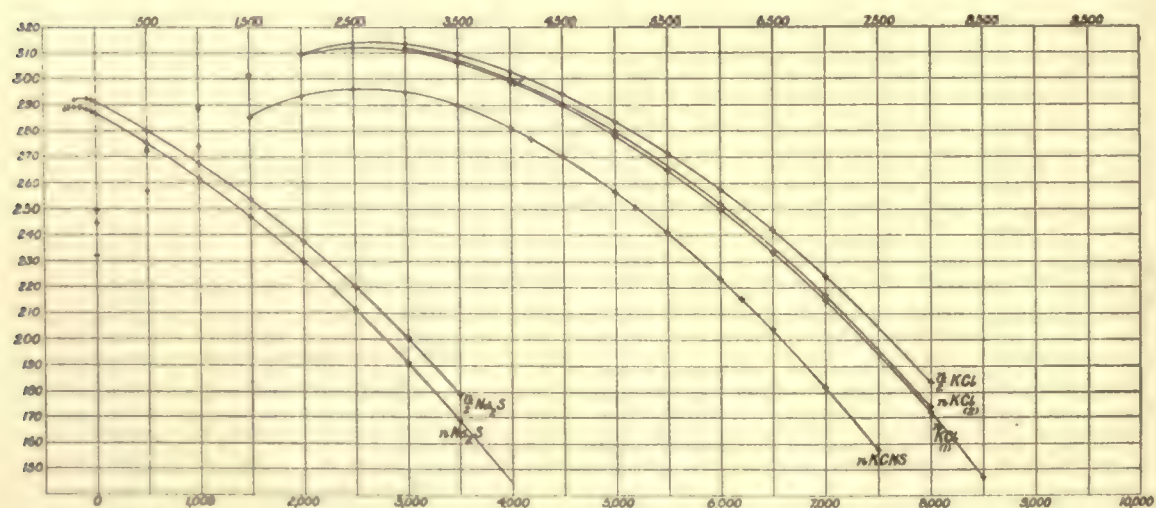
The numbers given show that, for dilute solutions at any rate, the double-layer theory gives results in complete accord with the Nernst-Planck view of the potential difference between KCl and KI. If it be considered that the former is *a priori* the more probable of the two hypotheses, the results may be taken to corroborate the

* Cf. NERNST, 'Zeits. f. Physik. Chemie,' 4, 1889.

E.M.F. applied to electrometer [1000 = 204 volt].	Surface tension readings.		Mean horizontal distance between curves. (a.)	Calculated E.M.F. of Hg KCl Na ₂ S Hg assuming P.D. between KCl and Na ₂ S to be negligible.	Observed E.M.F. of cell. Hg KCl Na ₂ S Hg (b.)
	n KCl.	n Na ₂ S.		volt.	
- 300		28.81	4600 ± 20		
- 250		28.89			
- 200		28.91			
- 150		28.9			
- 100		28.84			
- 50		28.78			
0	24.94	28.69			
500	27.3	27.5			
1000	28.95	26.18			
1500	30.1	24.68			4700 (max.)
2000	30.85	23.01			
2500	31.21	21.15		.9384	.9588 volt.
3000	31.11	19.15		± .0041	
3500	30.63	16.89			
4000	29.9	14.4			
4500	28.97	11.75			
5000	27.81			Calculated E.M.F. of cell, on ordinary Helmholtz theory, assuming P.D. be- tween liquids zero	
5500	26.5				
6000	25.01				
6500	23.39				
7000	21.5				
7500	19.41				
8000	17.19				
8500	14.7			.581 (approx.)	
9000	12.0				

E.M.F. applied to electrometer [1000 = .204 volt].	Surface tension readings.		Mean horizontal distance between curves. (a.)	Calculated E.M.F. of	Observed E.M.F. of cell.
	$\frac{n}{2}$ KCl.	$\frac{n}{2}$ Na ₂ S.		Hg KCl Na ₂ S Hg assuming P.D. between KCl and Na ₂ S to be negligible.	Hg KCl Na ₂ S Hg (b.)
				volt.	
- 200		29.19	4625 ± 25	.9435 ± .0051	4695 = .9578 volt.
- 100		29.23			
0	24.43	29.1			
500	27.2	28.02			
1000	28.89	26.79			
1500	30.1	25.39			
2000	30.96	23.8			
2500	31.4	22.0			
3000	31.33	20.08			
3500	30.95	17.91			
4000	30.29	15.59 †			
4500	29.41				
5000	28.39				
5500	27.18				
6000	25.78				
6500	24.2				
7000	22.43				
7500				Calculated E.M.F. of cell on Helmholtz theory, assuming P.D. between KCl and Na ₂ S zero.	
8000	18.37				
8500					
9000	13.41		.581 (approx.)		

Fig. 7.



The corresponding curves are given in fig. 7. In the case of the curves for potassium sulphocyanide and chloride it is clear that the results again agree with the hypothesis that in these solutions, when the potential difference between the solution

and the meniscus exceeds a certain value, the surface tensions are the same when the potential differences are equal. Conductivity data for KCNS are not available, so that it is impossible to say whether the ionic concentration is strictly the same for the two solutions; but if we may argue from the values for corresponding solutions of HCl and HCNS,* it would appear probable that the degree of dissociation of equally concentrated solutions of the salts is practically the same. The ionic velocities of the anions would also seem to be about the same.

THE RELATION BETWEEN THE NATURE OF THE KATION OF THE SOLUTION AND THE FORM OF THE ELECTROCAPILLARY CURVE.

Before the argument previously employed can be applied in the case of salts like KCl and Na_2S possessing different kations, it is necessary to assume that the effect of the kation upon the electro-capillary curve is independent of its chemical nature. The observations upon KCl, NaCl and HCl described below show that this is probably true. But apart from this there are uncertainties in the above experiments with sodium sulphide from which the others are free. It is difficult to prepare a standard solution of sodium sulphide. The solutions used were only approximately normal and half-normal. But besides this, the degree of dissociation of a normal sodium sulphide solution is probably considerably less than that of a normal potassium chloride solution. Hence the potential difference between the solutions is uncertain. Further, if the Na_2S solution is less concentrated than the corresponding KCl solution, the Na_2S descending curve will be relatively nearer the KCl descending curve than it would be if the ionic concentrations were equal (see below). This in itself might suffice to explain why the horizontal distance between the curves is less than that corresponding to the observed E.M.F. of the cell.

While it seems reasonable to suppose that if the uncertainty concerning the sodium sulphide were eliminated, the agreement would be as close as in the other cases, the experiments seem to leave little doubt as to which of the numbers quoted by NERNST (0.416 volt and zero) is nearer the true value of the potential difference between equally concentrated solutions of KCl and Na_2S .

Experiments with equally concentrated Solutions of Potassium and Sodium Chlorides.

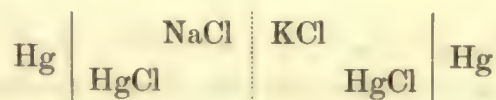
The following experiments show the probability that for equally concentrated solutions of potassium and sodium salts the kation produces the same effect upon the surface tension.

* OSTWALD, 'Journ. f. Prakt. Chemie,' 32, 1885.

E.M.F. applied.	Surface tension readings.					
	$\frac{n}{2}$ KCl.	$\frac{n}{2}$ NaCl.	$\frac{n}{10}$ KCl.	$\frac{n}{10}$ NaCl.	$\frac{n}{20}$ KCl.	$\frac{n}{20}$ NaCl.
0	24.09	24.31	24.78 †	24.99	25.1 †	25.22
500	26.99	27.08	27.4	27.42	27.4 †	27.36 †
1000	28.71	28.76	29.0	29.0	29.0 †	28.9 †
1500	29.95	30.01	30.2	30.21	30.18	30.1
2000	30.85 †	30.89	30.65	31.0	30.99	30.95
2500	31.25	31.31	31.33	31.44	31.45	31.41
3000	31.25	31.3	31.41	31.47	31.5	31.5
3500	30.9	30.93	31.2	31.2	31.3	31.27
4000	30.28	30.31	30.7	30.7	30.85	30.81
4500	29.42	29.5	29.99	30.0	30.2	30.19
5000	28.41	28.5	29.1	29.11	29.38	29.38
5500	27.27	27.3	28.0	28.10	28.32	28.35
6000	25.9	25.95	26.72	26.83	27.13	27.18
6500	24.32	24.4	25.33	25.43	25.79	25.83
7000	22.62	22.7	23.79	23.89	24.28	24.31
7500	20.7	20.82	22.0	22.15	22.6	22.7
8000	18.6	18.7	20.01	20.22	20.7	20.81
8500	16.33	16.5	17.9	18.15	18.62	18.79
9000	13.80	14.01	15.6	15.89	16.4	16.59
9500	14.0	14.2
Mean temperature.	17°	16°	17°	17°	16.7°	17°

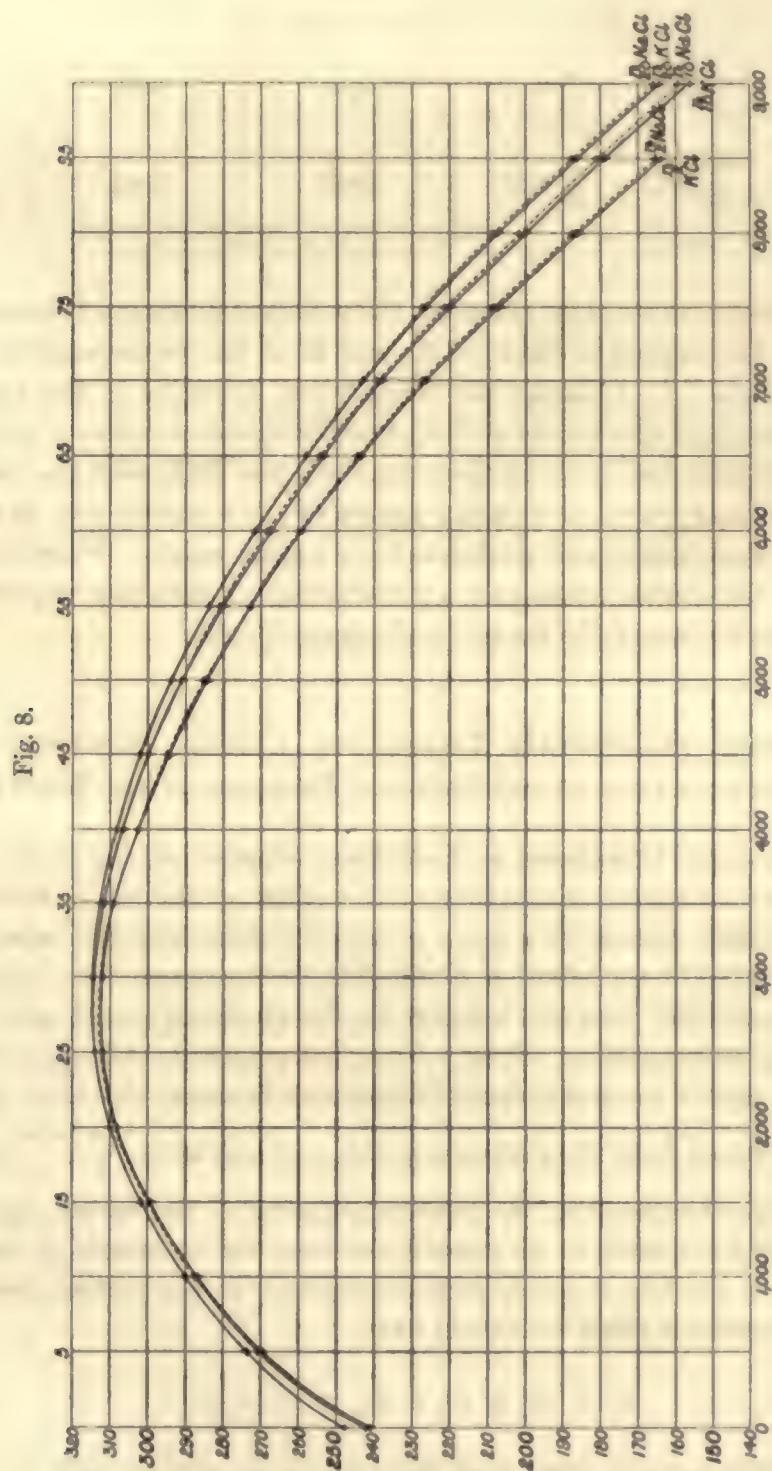
Fig. 8 shows the electro-capillary curves for half-normal, one-tenth normal, and one-twentieth normal solutions of potassium and sodium chlorides. In every case the mercury of the large electrode was covered with a layer of calomel before the introduction of the solution into the electrometer cell. The appreciable departure of the curves from one another at the lower surface tensions may be partly due to the appreciable effects of depolarization, since the conductivity of a KCl solution is about 20 per cent. greater than that of the corresponding NaCl solution. Apart from this departure at lower surface tensions, it is seen that the curves for corresponding solutions coincide within the limits of experimental error.

If we are to assume that the kations K and Na affect the surface tension in the same way, the E.M.F. of the cell of the type



should be merely the potential difference between the solutions.

The following are the calculated potential differences between the solutions and the observed E.M.F.s of the cells :—



		Observed.	Calculated.
$\frac{n}{10}$ NaCl	$\frac{n}{10}$ KCl	·0050	·0045
$\frac{n}{20}$ NaCl	$\frac{n}{20}$ KCl	·0045	·0045

From these results we see that, assuming the potential difference between the liquids is as calculated, the respective effects of Na and K on the electro-capillary curves are practically identical. To examine the effect when hydrogen is the kation, I have also performed similar experiments with hydrochloric acid of different strengths. The curves are practically the same as those for NaCl and KCl, with the exception that the hydrochloric acid curves eventually flatten out in a similar way to the sulphuric acid curve described earlier, and doubtless for a similar reason. Subsequently I hope to describe how the surface tension for a given potential difference depends upon the nature and concentration of the kation in the general case.

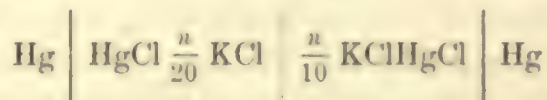
RELATION BETWEEN THE SURFACE TENSION FOR A GIVEN POTENTIAL DIFFERENCE AND THE CONCENTRATION OF THE SOLUTION EMPLOYED IN THE ELECTROMETER.

Following the same hypotheses as have been adopted above, it is easy to see, from the curves just given, the nature of the effect of the kation upon the surface tension. The surface tension for a given potential difference would seem to increase as the concentration of the solution diminishes, or conversely, for a given surface tension the potential fall from the solution to the electrode would seem to increase with diminishing concentration. Thus, to take the potassium chloride curves, suppose π_{n_2} , $\pi_{n_{10}}$, and $\pi_{n_{20}}$ are the natural potential differences between the large electrode and the solution (reckoned from the electrode to the solution) in the $\frac{n}{2}$, $\frac{n}{10}$, and $\frac{n}{20}$ solutions respectively. Considering the parallel portions of the curves, let π_{e_2} , $\pi_{e_{10}}$, and $\pi_{e_{20}}$ be the E.M.F.s required to be applied between the terminals in the respective cases, in order to produce a given surface tension. If the surface tension depends only on the electrostatic effect we should have

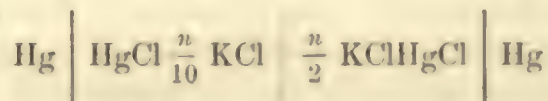
$$\pi_{e_2} - \pi_{n_2} = \pi_{e_{10}} - \pi_{n_{10}} = \pi_{e_{20}} - \pi_{n_{20}},$$

assuming, as in the previous cases, that there are no appreciable potential falls within the solutions, or that, if present, they are the same for all.

Suppose, now, that we measure the E.M.F.s of the cells



and



and find them to be π_2 and π_1 respectively. Then

$$\pi_2 = \pi_{n_{20}} - \pi_{n_{10}} + \pi_{n_{11}},$$

and

$$\pi_1 = \pi_{n_{10}} - \pi_{n_{11}} + \pi_{n_{12}},$$

where $\pi_{n_{11}}$ and $\pi_{n_{12}}$ are the potential differences between the unequally-concentrated solutions of KCl. Calculating the values of these by NERNST's formula we get

$$\pi_{n_{11}} = -0003 \text{ and } \pi_{n_{12}} = -0007.$$

The observed E.M.F.s of the cells were

$$\pi_2 = 0162 \text{ and } \pi_1 = 0359,$$

from which we see that (assuming NERNST's formula)

$$\pi_{n_{20}} - \pi_{n_{10}} = 0165,$$

and

$$\pi_{n_{10}} - \pi_{n_{11}} = 0366.$$

Now, from the curves

$$\pi_{e_{20}} - \pi_{e_{10}} = 0331 (\pm 0006)$$

and

$$\pi_{e_{10}} - \pi_{e_3} = 0670 (\pm 0006).$$

Hence, subtracting corresponding equations,

$$(\pi_{e_{20}} - \pi_{n_{20}}) - (\pi_{e_{10}} - \pi_{n_{10}}) = 0166$$

and

$$(\pi_{e_{10}} - \pi_{n_{10}}) - (\pi_{e_3} - \pi_{n_{11}}) = 0304,$$

whereas, if the surface tension variation had been due to a purely electrostatic effect,* we should have expected

$$(\pi_{e_{20}} - \pi_{n_{20}}) - (\pi_{e_{10}} - \pi_{n_{10}}) = 0$$

and

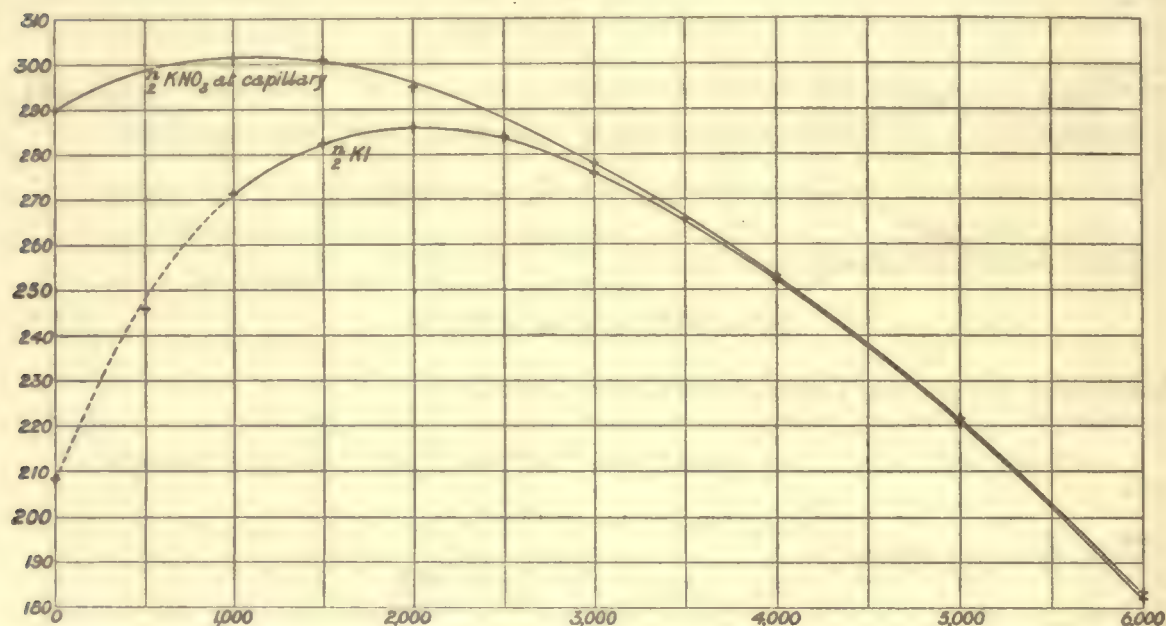
$$(\pi_{e_{10}} - \pi_{n_{10}}) - (\pi_{e_3} - \pi_{n_{11}}) = 0.$$

Disagreements of a similar kind are found when solutions of other strengths are examined. The same result can be very easily illustrated by means of the apparatus

* It can also be shown from the above and similar experiments that the surface tension variation in the descending branch cannot, in general, be a purely amalgam effect.

first described. Fig. 9 shows a curve for $\frac{1}{2}n$ KI, and another for the same solution, with the exception that the $\frac{1}{2}n$ KI, in which the capillary was first immersed, was replaced by $\frac{1}{2}n$ KNO₃, the degree of dissociation of which is 16 per cent. less than that of $\frac{1}{2}n$ KI. The calculated potential difference between $\frac{1}{2}n$ KNO₃ and $\frac{1}{2}n$ KI is rather less than .001 volt—an amount which would be barely perceptible on the scale to which the curves are drawn—so that the appreciable separation between the parallel portions of the curves is most probably due in part to the effect of the different concentrations of the potassium ions upon the surface tension.

Fig. 9.



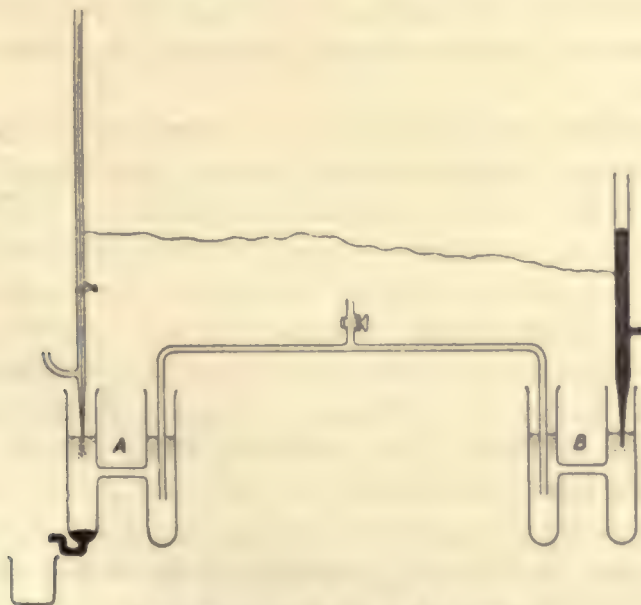
Since it is beyond the purpose of the present paper to deal with the quantitative nature of the possible ion effects upon the surface tension, it will be unnecessary to give further instances which show that the observed surface tension is, in general, partly determined by the chemical nature of the solution. It may, however, be remarked that there is nothing unusual in the supposition that as the potential difference reckoned from the solution to the electrode increases, the kation effect becomes pronounced, while conversely, when it diminishes, the anion effect becomes increasingly evident. For if the potential difference be altered in the above sense, through a sufficient range, we get an obvious combination of the mercury with the anion (and not simply a molecular layer of the compound) on the one hand, and with the kation (amalgam) on the other. Whether the formation of these compounds proceeds suddenly when the potential differences between the solution and the electrode reach certain amounts, or whether they are gradually led up to through intermediate stages in which the surface films contain only molecular quantities of the compounds, of gradually-increasing concentration, is a question concerning the answer to which we have imperfect knowledge.

RELATION BETWEEN THE ELECTROCAPILLARY CURVES FOR KCl AND KI AND DROPPING ELECTRODE MEASUREMENTS FOR SOLUTIONS OF THESE SALTS.

There is a point in connection with the explanation of dropping electrode phenomena which, as it is closely connected with the question of the potential difference between KCl and KI, may perhaps be mentioned here. If it be granted that the potential difference between $\frac{1}{2}n$ KCl and $\frac{1}{2}n$ KI can be considered negligible, it follows from the experiments described below that the potential difference between dropping mercury and KCl (under the conditions described by PASCHEN) is very different from that between dropping mercury and KI. And, at the same time, it follows that if the potential difference between a KCl solution and mercury is zero when the surface tension is a maximum, then, when the latter is a maximum in KI solution, the potential difference from the solution to the electrode has a considerable magnitude.

The result obtained by PASCHEN* (following up the experiments of OSTWALD†) for chlorides and iodides, among other salts, that the E.M.F. required to produce the maximum surface tension for a given solution is practically identical with the E.M.F. of a cell containing the same solution and having as electrodes a similar large mercury electrode to that used in the electrometer, and a dropping electrode of which the jet becomes discontinuous in the surface of the solution seems, at first sight, a striking confirmation of the Helmholtz theory of the electrometer. But, in fact, it is sufficient for this result that the potential difference between mercury and the solution when the surface tension is a maximum is the same as the potential difference between the dropping electrode (of the Paschen type) and the solution.

A dropping electrode and a capillary electrode were connected up as in the diagram.



* PASCHEN, 'Wied. Ann.,' 41, 1890.

† Cf. OSTWALD, 'Lehrbuch,' 2, 938.

The mercury of the dropping electrode fell into the tube A, which had a vertical fine adjustment attached, so that the position of the liquid in it could be varied with respect to the point of the dropping electrode. The capillary electrode was immersed in the liquid of the vessel B. The two electrodes were directly connected by a wire, and A and B were connected by a siphon tube.

The surface tension of the capillary electrode was measured under four different conditions, viz., when—

1. A and B were filled with $\frac{1}{2}n$ KCl.
2. A and B were filled with $\frac{1}{2}n$ KI.
3. A was filled with $\frac{1}{2}n$ KCl and B with $\frac{1}{2}n$ KI.
4. A was filled with $\frac{1}{2}n$ KI and B with $\frac{1}{2}n$ KCl.

The capillary electrode formed part of the electrometer previously described, and the curves which it gave for the $\frac{1}{2}n$ KI and the $\frac{1}{2}n$ KCl respectively were first determined.

From the behaviour of the capillary meniscus it was easy to observe when the dropping electrode jet broke in the surface of the solution in B. If the jet were completely immersed in the liquid and if, then, the latter were gradually lowered, the surface tension of the capillary electrode in general increased correspondingly to a maximum value and then changed in the same way as it did when the dropping electrode was absent—showing that the communication between the electrodes had then ceased.

In cases 1 and 2 the mercury in the capillary electrode assumed (within the limits of experimental error) its maximum surface tension when the dropping electrode broke in the surface of the liquid in A. Thus, for $\frac{1}{2}n$ KCl the readings lay between 31.3 and 31.35; for $\frac{1}{2}n$ KI the reading for several observations was 29.41. The corresponding readings of maximum surface tension for the electro-capillary curves were 31.4 and 29.43.

In case 3 the capillary surface tension lay between 26.38 and 26.31, and from the behaviour of the capillary meniscus when the drop electrode jet broke above the liquid surface—the surface tension gradually decreased—it was evident that this corresponded to a point on the ascending portion of the $\frac{1}{2}n$ KI curve. The horizontal distance between surface tensions of 29.43 and 26.35 on the $\frac{1}{2}n$ KI curve corresponds to a difference in the applied E.M.F. of about .28 volt. So that, if the potential difference between $\frac{1}{2}n$ KI and $\frac{1}{2}n$ KCl can be neglected, the conclusion from the above observations is that the potential difference between a Paschen electrode and the solution (reckoned from the latter to the former) is about .28 volt. greater when the solution is $\frac{1}{2}n$ KI than when it is $\frac{1}{2}n$ KCl.

The observation in case 3 is corroborated by that in case 4. In this case, when the electric contact between the dropping electrode and the solution was on the point of breaking, the observed surface tension of the capillary lay between 30.48 and 30.5;

but the surface tension increased when the contact broke, showing that the number given corresponded to a point on the descending branch of the KCl curve. The horizontal distance between the maximum and 30.5 on the KCl curve is approximately the same as in the former case. It corresponds to a potential difference of about .24 volt. Both results are somewhat uncertain, partly owing to the difficulty of determining the exact points of maximum surface tension on the capillary curves; but as the effects observed are so considerable, and as they are further corroborated by the results described below, there can be little doubt concerning their significance. The results can be further tested by experiments similar to PASCHEN's by measuring the E.M.F.s of cells of the type



in which the vertical arrow signifies the dropping electrode. The following approximate results were obtained ;—

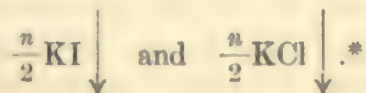
$$+ \text{Hg} \left| \frac{n}{2} \text{KCl} \right| \frac{n}{2} \text{KCl} \downarrow - = .522 \text{ volt.}$$

$$\text{Hg} \left| \frac{n}{2} \text{KCl} \right| \frac{n}{2} \text{KI} \downarrow = .784 \text{ ,,}$$

$$\text{Hg} \left| \frac{n}{2} \text{KI} \right| \frac{n}{2} \text{KI} \downarrow = .383 \text{ ,,}$$

$$\text{Hg} \left| \frac{n}{2} \text{KI} \right| \frac{n}{2} \text{KCl} \downarrow = .127 \text{ ,,}$$

The first and second results give .262 volt and the third and fourth give .256 volt as the difference between the potentials



The difference between the chemical effects during the dropping of mercury into

* I have found, since this was written, that G. MEYER ('Wied. Ann.,' vol. 56, 1895) measured the E.M.F. of a cell of the type $\frac{n}{2} \text{KCl} \left| \frac{n}{2} \text{KI} \right|$ and found it to be .284 volt. The observations described above are in accord with this result.

KI and KCl respectively is rendered evident if a drop of phenol phthalein solution is added to the solution in each experiment. The solution turns pink very much more rapidly in the case of the KI than in the case of the KCl, showing apparently that the combination of the mercury with the iodine is very much more rapid than with the chlorine, of the solution into which it is dropped, under the conditions described.

SUMMARY.

1. The Lippmann-Helmholtz theory of the capillary electrometer contains two assumptions.

2. The first assumption would apply to any electrolytic cell. A deduction from it, which would apply to any cell having a large and a small electrode, is that the variation of the potential difference at the capillary electrode of an electrometer is the same as that of the applied electromotive force.

In order to trace the relation between surface tension and potential difference on the view that this first assumption is correct, it is necessary to eliminate the possible effect of depolarization upon the form of the electrocapillary curve—*i.e.*, the curve which shows the relation between the surface tension and the applied electromotive force. A direct method of examining the depolarization current is described and applied. An estimate of the magnitude of the depolarization effect is given, and the circumstances under which the effect may become appreciable are discussed.

3. The second assumption of the Lippmann-Helmholtz theory, that the electrocapillary phenomena are controlled by a simple variation of the electrostatic surface energy, leads to two conclusions, each of which is beset with difficulties.

(*a.*) The form of the electrocapillary curve is remarkably dependent upon the nature and concentration of the electrolyte, and depolarization is quite insufficient to account for the dependence.

(*b.*) The conclusion that the potential difference between the solution and the capillary electrode is zero when the surface tension has its maximum value, leads to the necessity for assuming large potential differences between certain solutions.

4. The hypothesis that the potential difference between equally concentrated solutions of potassium chloride and iodide is negligible possesses a high degree of probability. It has been shown by previous observers that if this hypothesis be true the points of maximum surface tension on the electrocapillary curves for the above solutions cannot have the significance which HELMHOLTZ's theory gives them.

It is shown in the paper that the first hypothesis of the Lippmann-Helmholtz theory is in striking accord with this hypothesis concerning the potential difference between KCl and KI when the very definite "descending" branches of the electrocapillary curves are considered.

5. If both the hypotheses just mentioned be true, we get the result that the surface tension of mercury (for a certain range of potential differences) in two solutions

is the same for a given potential difference between the mercury and the respective solutions, if the solutions are equally concentrated and possess the same kation.

6. An extension of this result shows that it is indifferent whether the kation be K, Na, or H.

7. The relation found for the KCl and KI curves can be extended to the other known cases in which the electrometer curves and liquid potential difference calculations seem to be contradictory, in such a way as to account for the apparent contradiction. Several of the cases are examined.

8. The results in 4, 5, and 6 would give a direct and accurate method of finding the potential differences between equally concentrated solutions, and could be extended to the case of solutions of different concentrations.

9. The probability that the electrocapillary curves are never completely free from influences other than electrostatic is shown by an examination of the relations between the curves for unequally concentrated solutions of the same salt.

10. In confirmation of results obtained by G. MEYER, in a slightly different way, it is shown that if the potential difference between KCl and KI is very small, the potential fall from a half-normal solution of KI to a dropping electrode of the Paschen type is about a quarter of a volt greater than that from a half-normal solution of KCl to the same electrode.

In the same way the potential fall from KI to mercury when the surface tension is a maximum is about a quarter of a volt greater than that from KCl to mercury when the tension of the surface separating the solution from the mercury is a maximum.

These results follow from direct observations with dropping electrodes, and give further support to the view that the first assumption of the Lippmann-Helmholtz theory is true and that the second is not.

III. *The Electrical Conductivity and Luminosity of Flames containing Vaporised Salts.*

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Communicated by Sir H. E. ROSCOE, *F.R.S.*

Received October 24,—Read November 17, 1898,—Revised February 9, 1899.

THE colour imparted to flames by the salts of an alkali metal is generally considered to be due to the metal existing in the state of incandescent vapour, but there does not appear to be any settled opinion as to the process by which the metal is set free from its salts. It is frequently assumed that the high temperature reigning in the flame dissociates the salt. There is, however, little, if any, independent evidence in favour of this view. Another explanation ascribes the liberation of metal to chemical decomposition. Thus, in the case of sodium chloride introduced into the flame of a Bunsen burner consuming coal-gas, it would be supposed that in the first instance the water vapour present would act in accordance with the following equation :—



The sodium hydrate (or possibly oxide) so produced would then be deprived of its oxygen by reducing gases (hydrogen, hydrocarbon, carbon monoxide) existing in the flame. A somewhat similar explanation would have to be applied to the flames of hydrogen, carbon monoxide, and cyanogen, though, in the case of the last two gases, the steps of the processes are still more hypothetical.

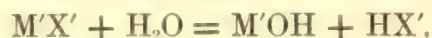
It is a noteworthy fact that the coloration of flames by alkali salts extends up to, and even beyond, the outer margin of the visible region of combustion, where the flame gases are usually considered to be fully oxidised and where free atmospheric oxygen exists. In such parts of a flame metals, much less oxidisable than the alkali metals, are rapidly oxidised when in the massive state. A copper wire, for example, becomes incrustated with oxide in a region where yellow light is abundantly emitted from a salted flame. A superoxygenated oxy-hydrogen flame is also coloured yellow by salt.

In discussing these facts* one of us was led to consider whether an alternative explanation might not be sought from some conclusions, derived by Professor ARRHENIUS, from a study of the electrical conductivity of salt vapours in flames.†

* 'Philosophical Magazine' (V.), vol. 37, 245, 1894.

† 'Wied. Ann.,' vol. 42, 18, 1891.

From the analogy stated to exist between dilute solutions of solids and matter in the gaseous state, and from his own theory that in dilute solutions electrolytes are in greater or less degree dissociated into their ions, ARRHENIUS was led to suppose that the vapour of electrolytes distributed in small concentration throughout a gas would likewise be electrolytically dissociated. He considers his experimental results to harmonise with this view. He supposes that when an alkali salt is introduced into a coal-gas flame the large excess of water vapour present converts the salt into a hydroxide, in accordance with the following equation :—



The hydroxide is then supposed to dissociate to a certain extent into its ions.

Now, according to the electrolytic theory of solution, a free ion may, in virtue of its electric charge, be characterised by properties totally different from those pertaining to the ordinary chemical atom. Thus, in a dilute solution of sodium chloride, sodium ions may persist in presence of water. If we accept the results and views of ARRHENIUS, we might suppose that in a flame coloured by an alkali salt, the metal is liberated as an ion, and as such may persist in a strongly oxidising medium of flame gases. Such an explanation would avoid the difficulties attending the more usually adopted views.

Another consideration appeared to favour the hypothesis suggested to us by the results of ARRHENIUS. According to him the conductivity of a salt vapour is proportional to the square root of its concentration in the flame. Now GOUY has shown ('Ann. Chim. Phys.,' 18, 5, 1879), that the luminosity of a flame coloured by an alkali salt is also within certain limits nearly proportional to the square root of its concentration in the flame.

The parallelism of these numerical relationships would obviously find a simple explanation in the event of the luminosity and electrical conductivity being both dependent on the presence of free ions.

The importance of these deductions as affecting spectrum analysis decided us to undertake an experimental investigation of the subject, and we were the more inclined to this from the belief that we had at hand an apparatus capable of giving accurate results. Besides this, a close examination of the results of ARRHENIUS revealed some apparent discrepancies that detract from the weight of his conclusions.*

The apparatus that we designed to employ was that used in other investigations of flame (SMITHELLS, 'Phil. Mag.' (V.), 39, 123 (1895)). This apparatus permits of the wide separation of the two cones that constitute the non-luminous flame of a Bunsen burner, and it was thought that the interconal space which, in the apparatus, is quite shielded from draughts, would afford a particularly favourable means of

* In his paper (*loc. cit.*) on p. 33, ARRHENIUS, dealing with the relation of conductivity to electromotive force, gives a set of galvanometer readings for an electromotive force of .2 Daniell. Later in the paper, on p. 36, when dealing with the relation of electromotive force to concentration, another set of readings,

obtaining constant conditions during the experiments. In other respects it was proposed to use arrangements similar to those of ARRHENIUS.

Preliminary experiments with the apparatus showed at once that numerous precautions were necessary to secure constant results, and it was only after many months of trial and the accumulation and rejection of series of measurements that the apparatus was finally brought into a reliable working condition.

The experiments have been confined to salts of the alkali metals. The relative conductivities of flames into which the salts were projected were determined and the experiments were designed to show :

- I. The relation between conductivity and electromotive force.
- II. The relation between the conductivity and the amount of salt present.
- III. The relation between the conductivities of equivalent quantities of various salts of the same metal.
- IV. The comparative conductivity of equivalent quantities of the salts of different metals.
- V. The behaviour of the same salts in different flames.

From these results, conclusions are drawn respecting the primary object of the investigation, which was to discover whether the coloration of flames, and their electrical conductivity when containing vaporised salts, are due to a common cause.

Description of Apparatus and Method of Working.

The apparatus employed in this investigation consisted essentially of an arrangement for producing a Bunsen flame with separated cones, into which salt solutions could be introduced as a fine spray along with the mixed coal-gas and air. A pair

also for an electromotive force of .2 Daniell, is given. The following are extracts from the two sets of readings :—

	Normal NaCl.	$\frac{N}{4}$ RbCl.	$\frac{N}{16}$ CsCl.	Normal LiCl.	Normal Na $\overline{\text{Ac}}$.
From Table 1	25.8	215	152	5.4	30.0
„ Table 2	41.0	161	121	8.1	30.2
Per cent. difference . .	59	- 26	- 20	50	0.6

The fact that the readings are not identical is not important, as ARRHENIUS expressly states that his electrodes suffered change in course of the investigation ; but it will be observed that the differences are quite capricious. Thus the second reading for sodium chloride is 60 per cent. greater than the first, whilst for rubidium chloride the second reading is 25 per cent. less than the first. We are unable to conjecture any satisfactory explanation of these discrepancies.

of electrodes was placed between the cones, and the electric currents between them measured under various E.M.F.s.

It was found that any unsteadiness of the flame produced considerable and irregular deflections of the galvanometer which prevented the current from being measured in a satisfactory manner. The steadiness of the flame could be judged readily by observing the lower cone, which, in consequence of the large amount of air mixed with the gas (about 5 vols. air to 1 of coal-gas) in order to produce separation of the cones, was very sharply defined. This cone in our earlier experiments could be seen to oscillate up and down and from side to side.

With a view to reducing this oscillation to a minimum, so as to obtain a steady galvanometer deflection, care was taken to regulate the quantity and pressure of the gas and air supplies with as much nicety as possible. This greatly diminished the oscillations, and a further great improvement was effected by admitting the gas close to the nozzle of the sprayer, so as to produce a more perfect admixture.

With the arrangements finally adopted, it was found that the values obtained for any particular solution remained approximately constant during the whole period covered by our experiments.

The air was supplied under high pressure by means of a Westinghouse air-pump, the amount of air used being but a small fraction of what the pump could supply. The air was filtered through a long cotton-wool plug, P (fig. 1), and a first adjustment of the supply was afforded by a tap close to a small mercury manometer, M. The excess of air thus diverted blew off through a tube dipping 160 centims. below the surface of water contained in the cylinder, C. The air to be used was next passed into an iron drum, D, of 500 litres capacity, in order to damp down any pulsations of pressure.

The coal-gas was regulated by admission into a large gas holder, G, whence it passed through a micrometer screw tap, S, to the flame tube.

The adjustment of the sprayer is a matter of great importance, as the constancy of its action determines mainly the accuracy of the experiments. To obtain constant action it is necessary to work the sprayer with a much greater air supply than is just sufficient to actuate it, otherwise small variations in the pressure produce considerable changes in the amount of spray produced. Besides this, a strong air supply, producing a large amount of spray, permits the use of more dilute solutions than would otherwise be necessary. The difficulty of obtaining reliable results increases rapidly as the concentration of the solutions is increased.

The arrangement of the sprayer finally adopted is shown in fig. 2. The outer tube, O, was blown like a test-tube, with a hole 2 millims. in diameter. The inner tube, I, which was made narrow, so as to leave as much free space as possible, was joined to a wider tube, and, after exact adjustment, this was cemented to the outer tube. The sprayer was fitted into a large paraffined cork, C, which closed the end of the tubulated

glass cylinder, and in this most of the coarse spray was deposited, running back into the reservoir of solution.

The solution in the reservoir, R, was always adjusted to a constant level, which was about 1 centim. below the nozzle of the sprayer.

The air supply from the iron drum, D (fig. 1), was passed through a flask, F, half

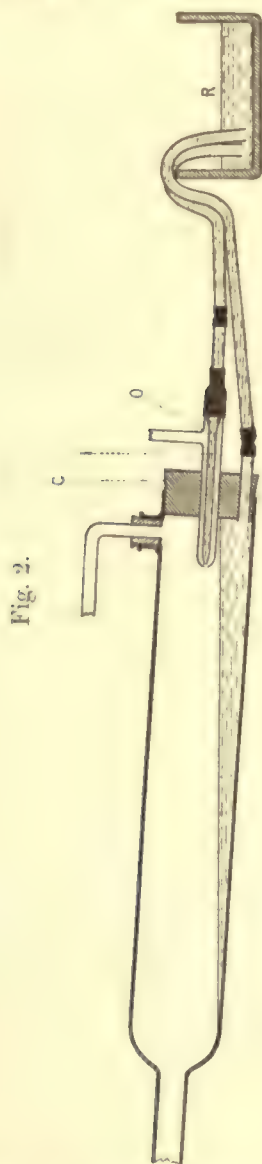


Fig. 2.

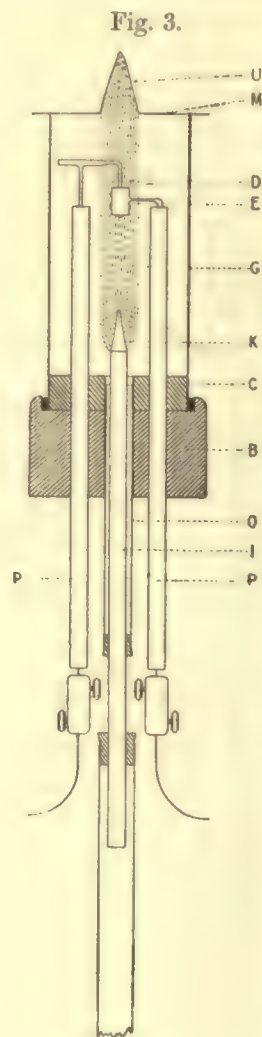


Fig. 3.

full of water, which, being gently warmed, served to saturate the air with moisture. Any excess of moisture was condensed in the long tube and in two empty bottles, B. A water manometer, W, was connected to a branch between these bottles, and the air supply regulated so that this indicated 118.5 centims., the variations not exceeding 1 or 2 millims.

The gas pressure was measured by a multiplying differential manometer, L, contain-

ing two immiscible liquids of nearly equal specific gravity. A pressure of 1 centim. of water corresponded to a motion of 10 centims. in the surface of separation. The pressure actually employed produced a motion of the surface of separation of 18.65 centims. A constriction was made in the gas supply tube just before it joined the air, so that the pressure should be great enough to be measured with accuracy. The variation in the gas pressure during the experiments did not exceed .25 per cent.

It was found advisable to pass the mixture of gas, air, and spray through a considerable length of apparatus, in order to allow only very fine spray to get to the flame, and to allow time for the thorough mixing of gas and air, on which the steadiness of the flame so greatly depends. The arrangement of this part of the apparatus is obvious from fig. 1.

The cone-separating apparatus and electrodes are shown in fig. 3. The gaseous mixture and spray pass up through the central tube, I, made of thin brass. On this tube the upper part of the apparatus could be slid up or down, so as to bring the electrodes to any desired height above the mouth of the tube. The hard wood block, B, was provided with three screws for centring the tube. A wider brass tube, O, was fixed into the block, and was provided at the lower end with a cork, through which the inner tube could slide.

A large cork, C, was cemented on to the wooden block in order to keep the glass cylinder, G, in position. The lower edge of the cylinder fitted into a groove in the block and was trapped with mercury.

A mica plate, M, kept in position by brass clips and pierced in the centre by a hole 2.2 centims. in diameter, was placed on the top of the glass cylinder. The electrodes were supported by two rigid porcelain tubes, P, fixed into the wood block by a packing of fusible metal. The electrodes consisted of two concentric cylinders of platinum iridium alloy. The outside cylinder, E, was supported by a wire of the same material, .5 millim. in diameter, thickened after a distance of 1.5 centims. to 2 millims., and bent at right angles so that it reached for 3 centims. down the porcelain tube, where it was joined to a platinum wire. By means of a cross-piece fitting into a V-shaped groove at the top of the porcelain tube, this attachment of the electrode was kept in a fixed position. The inner electrode cylinder, D, was supported in a similar way. The lower end of this cylinder was provided with conical cap so as to avoid the formation of eddies in the gas stream.

The dimensions of the electrodes were—

Height of cylinders	1.575 centims.
Inside diameter of outer cylinder.875 centim.
Outside diameter of inner cylinder450 ..

The electrodes were set up so as to be concentric and co-axial with the flame, so that a symmetrical region of flame gases was included.

In our preliminary experiments we tried electrodes consisting of platinum foil

suspended by stretched platinum wires, according to the plan of ARRHENIUS. We found them unsatisfactory owing to the slackening of the wires after heating. We also tried thicker platinum plates attached to thin platinum rods and supported by porcelain tubes. We believe, however, that our final arrangement was preferable in point of rigidity and in including a symmetrical zone of gases for measurement.

A vertical millimetre scale, H (fig. 1), fixed behind the glass cylinder, enabled the height of the electrodes and of the inner cone of flame, K, to be read by means of a cathetometer telescope.

The source of electricity used by us consisted usually of three accumulators. A German silver wire, 1.5 millims. in diameter and 20 metres long, carefully calibrated, was stretched four times along a bench over a millimetre scale, E. By making contact with two heavy three-legged contact-pieces at two points, any E.M.F. up to 5.7 volts could be taken off this wire.

The current in the circuit through the flame was measured by a Kelvin astatic reflecting galvanometer, K, of 5600 ohms resistance, provided with a shunt box, X. In every case in taking a reading the current through the galvanometer was reversed and the mean deflection taken. The sensibility of the galvanometer, as we used it, was about 2.85×10^{-9} ampere for one scale division. All connecting wires were supported on glass rods fixed in paraffin blocks.

The E.M.F. given by the stretched wire was compared on all occasions with that given by a standard Clark element, and the sensibility of the galvanometer was repeatedly determined.

In some earlier experiments higher E.M.F.s were obtained by means of Leclanché cells up to thirty in number.

In the following pages the measurement of current strength is always given, except where otherwise specified, in terms of 10^{-7} ampere unit.

Method of making an Experiment.

In beginning an experiment the tubulated cylinder, T (fig. 1), was removed, and, together with the sprayer, washed well with distilled water and dried by a current of air.

The cylinder was then replaced and the reservoir, R, filled with the solution to be investigated.

Any salt which in a previous experiment had deposited on the flame tube was removed, and the cylinder, G (fig. 2), and mica plate washed and dried. The gas was then turned on and, after an interval, lighted above the mica plate. Air was next supplied until the sprayer came into action, when the level in the reservoir, R, was adjusted. When the flame had become non-luminous the mica plate was removed, so that the whole flame descended and burnt at the mouth of the flame tube. As soon as the air had reached the right pressure the mica plate was replaced, whereupon the outer cone, U (fig. 3), of the Bunsen flame rose and burned above the mica.

When distilled water is sprayed the two cones of flame are blue in colour; the inner one is extremely thin and bright. The cones are free from the reddish tints (due to dust) seen in an ordinary Bunsen burner. The interconal space (dotted in fig. 3) emits no light.

When a salt solution is sprayed the characteristic radiation appears at the surface of the inner cone and extends over the dotted region shown in fig. 3, forming an approximately cylindrical column 3 centims. in diameter, in which the electrodes are symmetrically immersed. The electrodes become bright red, the inner one being rather brighter than the outer one is on the outside.

After about ten minutes spraying the measurements were commenced. The highest E.M.F. was usually applied first and lower ones substituted successively. At the end of a series the earlier observations were repeated.

The current was measured, and then reversed and measured again, and as the current was also taken in both directions through the galvanometer, four readings were obtained, and of these the average was taken.

During an experiment one observer watched the manometers on the air and gas supply, whilst the other took the galvanometer readings.

In working with strong solutions great care is necessary to keep the air in the right hygrometric state. If it is not moist enough, salt crystals deposit on the nozzle of the sprayer and impede the air supply; whilst if it is too moist, drops of water are deposited, with the same effect.

In our earlier experiments with sprayers, in which the outer tube was conical at the end, much trouble came from these sources; the trouble was much less with the form of sprayer described above.

To gauge the constancy of the apparatus we employed a $\frac{1}{10}$ normal solution of potassium bromide. The following readings for an E.M.F. of 5.6 volts, taken at intervals during three months, will give an idea of degree of constancy attained:—

21.1, 21.3, 20.7, 21.8, 21.6, 22.9, 22.1, 21.7: Mean 21.4.

Other solutions were used, from time to time, as a control. When abnormal values were obtained, an examination of the apparatus always disclosed some slight remediable defect.

Conductivity of the Free Flame.

To obtain the true conducting power of a vaporised salt it is necessary, in every case, to make a correction in order to eliminate that portion of the observed conductivity which is due to the flame gases. For this purpose we made, in the first instance, a series of observations on the conductivity of the flame, with the addition only of the spray of distilled water.

In making these experiments, it was found necessary to change the distilled water at frequent intervals, otherwise the apparent conductivity steadily increased owing, it

would appear, to solution of the glass. The quantity dissolved is, of course, small, but still quite sufficient to make itself felt. The conductivity of the flame gases alone, is, it must be remembered, extremely small in comparison with that of a flame containing the spray of $\frac{1}{1000}$ normal solution of a potassium salt.*

The following table gives the conductivity of the flame gases with distilled water spray for several electromotive forces:—

E.M.F. in volts . .	5.66	2.52	1.09	.803	.521	.230.
Current547	.313	.226	.177	.118	.056.

These results are plotted in Curve V, p. 110, the ordinates being multiplied by 10.

The above values were checked from time to time during our work. The agreement was always well within the limits of accuracy required, and consequently we have used these values in all cases to represent the conductivity of the free flame, subtracting them from the gross readings given by salt solutions to obtain the conductivity of the salt vapour itself.

ARRHENIUS, in his experiments on this subject, noticed an increased conductivity of the free flame immediately after a salt solution had been sprayed. He attributed it to a deposition of salt on the electrodes, the deposit remaining on the electrodes for some time after the spray of salt solution had been stopped. The effect in question was not important in the case of salts of the alkali metals on account of their ready volatility.

In our experiments we noticed this effect, but we believe that in our apparatus with the salts used by us it was fully accounted for by the fact that after the spray of salt had been replaced by one of water, salt spray lingered for some time in the apparatus between the sprayer and the flame tube. We noticed that the flame remained coloured below the electrodes, and that as the colour faded the galvanometer deflection fell steadily to the normal value. We have therefore used the normal value as the true correction. Even if our explanation of the higher value, found immediately after stopping the salt spray, is incomplete, the arbitrariness in our case of taking any other value than the normal one as the correction, would forbid us attempting further refinement, where, as a matter of fact, the difference involved could not seriously affect our final results.

Unipolar Conduction.

It has long been known that unipolar conduction is shown to a marked extent in the case of flame gases, that is to say the current passes from one electrode to the other more easily in one direction than in the reverse direction. The following table

* SCHALLER has shown ('Zeit. Phys. Chem.,' 25, 497, 1898) that pure water acts so rapidly on glass vessels as to forbid their use in conductivity experiments, but that with salt solutions, even of very small concentration, the solvent action is not sufficient to introduce sensible error.

gives the results obtained by us in an early series of experiments, where the electrodes consisted of two platinum plates equal in size and placed as symmetrically as possible in the flame. A $\frac{1}{10}$ normal solution of KCl was used in these experiments :—

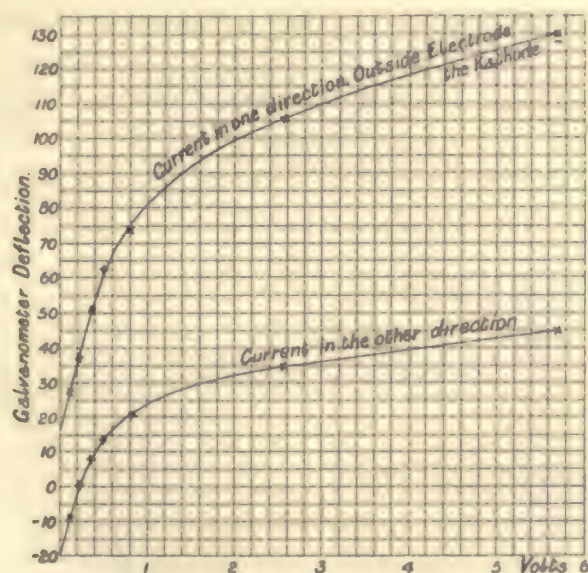
E.M.F. in volts.	Galvanometer deflection.	Galvanometer deflection (current reversed).
43.5	+ 39.7	- 48.8
29.0	+ 33.2	- 41.0
14.5	+ 24.7	- 29.3
7.3	+ 19.4	- 23.0
2.9	+ 15.1	- 16.9
1.5	+ 12.8	- 14.2

With the cylindrical electrodes used in our later experiments the electrode surfaces are of different size, and with these the unipolar effect is much greater. The following is a table for $\frac{1}{10}$ normal KCl solution :—

E.M.F. in volts.	Galvanometer deflection.	Galvanometer deflection (current reversed).
5.74	+ 81.3	- 22.5
2.56	+ 69.5	- 18.7
.815	+ 52.8	- 14.1
.378	+ 35.2	- 11.1
.116	+ 12.1	- 3.0

These results are plotted in Curve I.

Curve I.



Unipolar conduction ($\frac{N}{20}$ KNO₃ solution sprayed).

We do not propose to enter into a discussion of the cause of this unipolar conduction, which has already been the subject of frequent, but not very fruitful, research. If it be due to the assymetry of the electrode system, either in regard to their size or position in the flame, and if it be connected with the well-known influence of ultra-violet light or of a high temperature in facilitating the discharge of negative electricity, the circumstances of our experiments offer no obstacle to such an explanation. But they do not throw any fresh light on the phenomenon, and it is outside the scope of our enquiries to discuss it.

Concentration of Salt Vapour in the Flame.

To obtain an estimate of the quantity of salt vapour entering the flame in our experiments, we adopted the method used by ARRHENIUS.

The cone separating apparatus was removed, and the flame obtained at the orifice of the tube I (fig. 3). A bead of sodium sulphate was held in the flame for a measured interval of time, during which the light intensity was compared photometrically with that of a standard candle. The loss in weight of the bead was determined. By spraying a sodium sulphate solution of suitable strength in our apparatus, a flame of light intensity equal to that containing the bead was obtained.

The following numbers give the results. They afford, at the same time, a confirmation of the statement of GOUY, that above a certain limit the light intensity of a flame coloured by the vapour of an alkali salt varies approximately as the square root of the amount of salt introduced.

Experiment 1. Loss of weight of bead per minute, '00161 gram. Intensity of light, 1.56.

Experiment 2. Loss of weight of bead per minute, '00325 gram. Intensity of light, 2.00.

Experiment 3. Solution sprayed $\frac{1}{2}$ normal sodium sulphate. Intensity of light, 1.53.

Experiment 4. Solution sprayed $\frac{1}{5}$ normal sodium sulphate. Intensity of light, .95.

From Experiments 1 and 2 we have—

Ratio of light intensities	1.3
Square root of ratio of concentrations	1.4

From Experiments 3 and 4—

Ratio of light intensities	1.6
Square root of ratio of concentrations	1.6

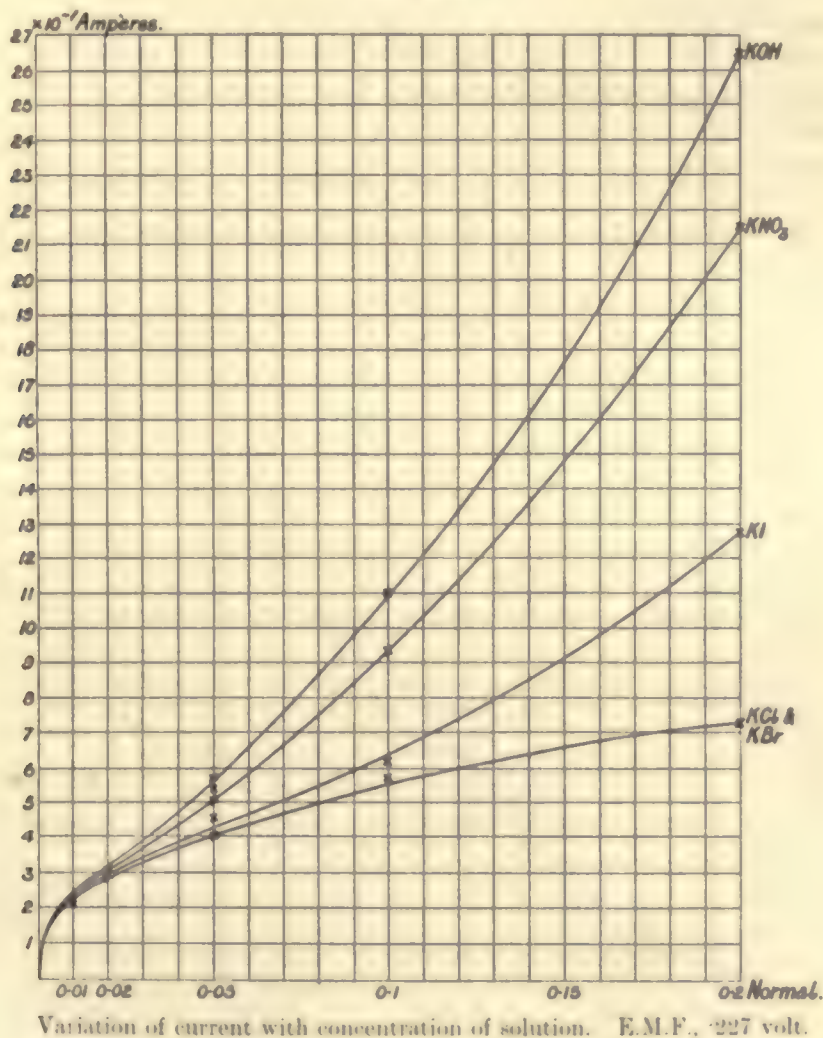
The amount of salt supplied to the flame per minute by the half normal sodium sulphate solution may therefore be taken as '0016 gram, and as a rough approxima-

tion we may conclude that the number of gram molecules supplied to the flame per minute is*

$$\frac{0.016}{71} \times 2 = 4.5 \times 10^{-6}.$$

It is important to note that we were able to investigate the conductivity of salt vapours at much greater concentrations in the flame than was done by ARRHENIUS, and, as will appear in what follows, the results at high concentrations are very different from those obtained at the lower ones.

Curve II.



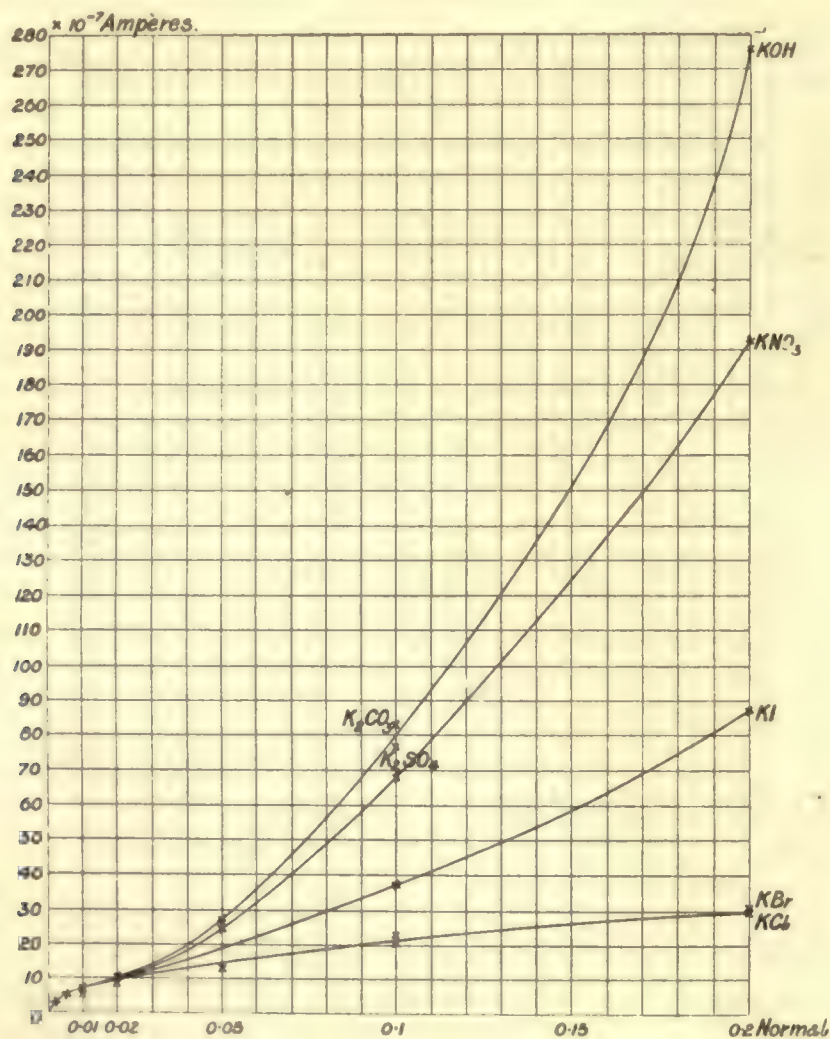
* This estimate, which has no pretensions to exactness, was made chiefly in order to inform us how our experiments compared with those of ARRHENIUS in respect to the concentration of salt in the flame. In his experiments a normal solution sent into the flame 26×10^{-2} gram molecule of salt per minute. In our apparatus an $\frac{1}{4}$ normal solution would yield this amount of salt. We confirmed this result by comparison of the conductivity numbers for salt solutions.

Relation of Conductivity to Concentration of Solution and to the Nature of the Salt.

Experiments with solutions of the various salts in different concentrations show that the relation between conductivity and concentration of salt vapour in the flame is not of a very simple nature.

Marked differences of conductivity are shown by salts according to their electro-positive constituent, and under certain conditions, also, according to their electro-negative constituent.

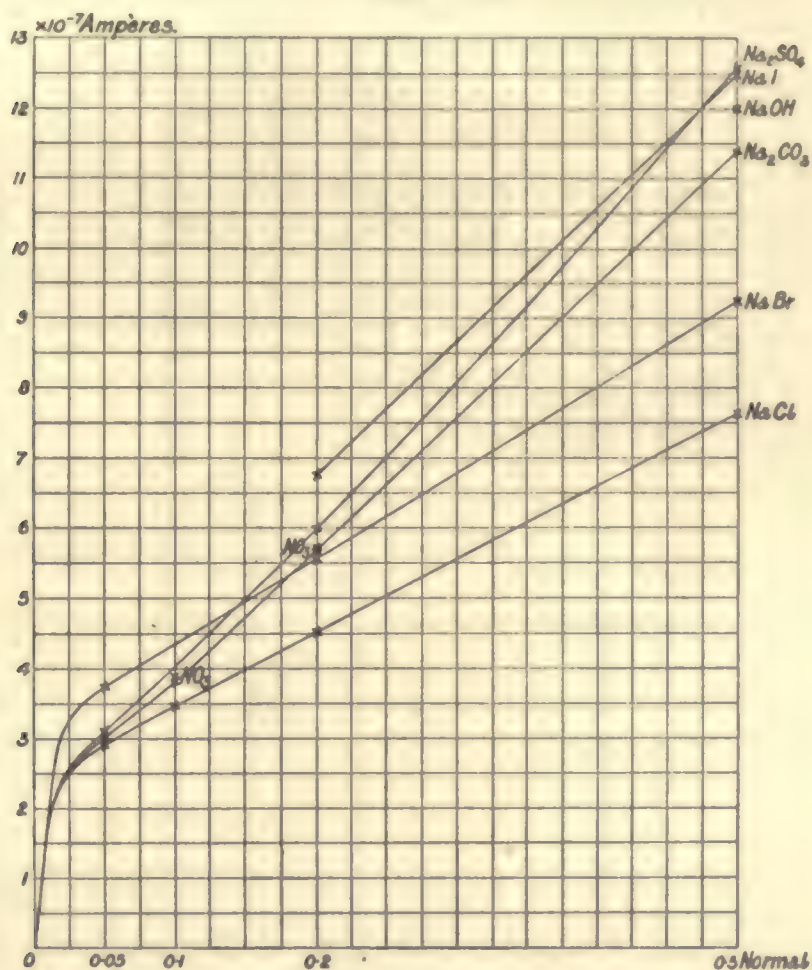
Curve III.



Variation of current with concentration of solution. E.M.F., 5.60 volts.

Curves II, III, and IV show clearly the variation of conducting power with concentration, the ordinates and abscissæ being respectively current strength and concentration.

Curve IV.



Variation of current with concentration of solution. E.M.F., 5.60 volts.

In the following table the experimental numbers are given for three different electromotive forces. In all cases the numbers have been corrected for the conducting power of the free flame.

Concentration of solution.	E.M.F.	KCl.	KBr.	KClO ₃ .	KI.	KNO ₃ .	$\frac{N}{2}$ K ₂ SO ₄ .	$\frac{N}{2}$ K ₂ CO ₃ .	KOH.
·2 normal	5·60	31·9	31·4	30·5	86·5	193	276
	·795	18·9	20·1	16·8	43·2	70·8	82·6
	·227	7·34	7·32	6·62	12·8	21·6	26·6
·1	5·60	21·0	21·4	...	37·8	68·3	83·3	76·4	
	·795	13·4	12·4	...	21·3	29·3	33·4	35·4	
	·227	5·75	5·74	...	6·2	9·35	11·0	11·2	
·05	5·60	14·1	14·7	12·9	22·8	24·5	27·5	27·6	24·1
	·795	9·23	10·3	8·35	12·8	13·2	13·8	14·2	12·8
	·227	4·0	4·13	3·81	4·6	5·1	5·71	5·43	5·4
·02	5·60	8·93	10·2			
	·795	6·09	6·63			
	·227	2·97	3·15			
·01	5·60	6·02	6·97	6·77	6·99	7·06	6·33	6·00	6·1
	·795	4·27	4·90	4·69	4·78	4·84	4·56	4·30	4·05
	·227	2·17	2·23	2·31	1·97	2·47	2·30	2·20	1·86
·005	5·60	5·47	5·27			
·002	4·03	...	3·89	3·73	
			2·80	...	2·73	2·59	
			1·50	...	1·24	1·45	

Concentration of solution.	E.M.F.	NaF.	NaCl.	NaBr.	NaI.	NaNO ₃ .	$\frac{N}{2}$ Na ₂ SO ₄ .	$\frac{N}{2}$ Na ₂ CO ₃ .	NaOH.
·5 normal	5·60	8·98	7·66	9·24	12·5	...	12·6	11·4	12·0
	·795	4·78	5·37	5·38	5·83	...	6·64	6·60	6·20
	·227	2·00	2·07	2·11	2·21	...	2·49	2·45	2·61
·2	5·60	4·03	4·54	5·56	6·72	5·73	5·99	5·67	
	·795	2·65	3·14	3·32	3·36	3·77	3·75	3·64	
	·227	1·39	1·42	1·41	1·39	1·85	1·61	1·71	
·1	5·60	...	3·49	3·88	...	3·78	
	·795	...	2·45	2·67	...	2·65	
	·227	...	1·15	1·30	...	1·30	
·05	5·60	2·91	2·95	3·76	3·09	3·02	3·00
	·795	2·08	2·21	2·50	2·16	2·12	2·07
	·227	·98	1·05	·97	·96	·97	·98

Concentration of solution.	E.M.F.	LiCl.	LiNO ₃ .	RbCl.	RbNO ₃ .	CsCl.	CsNO ₃ .	HCl.
·5 normal	5·60	1·88	2·28	1·08
	·795	1·09	1·59	
	·227	·56	·89	·35
·1	5·60	1·29	1·47	41·4	213·0	123	303	
	·795	·87	·99	26·4	82·4	60·5	115	
	·227	·41	·53	11·3	25·9	22·2	36·6	
·02	5·60	14·8	19·4	17·6	20·1	
	·795	9·65	11·6	11·7	13·1	
	·227	4·71	5·14	5·9	6·2	
·004	5·60	6·46	5·44	7·98	7·86	
	·795	4·51	4·18	5·70	5·51	
	·227	2·41	2·26	3·02	2·97	

The foregoing tables show—

- I. That at small concentrations equivalent solutions of all salts of the same metal impart the same conducting power to the flame.
- II. That at higher concentrations the equality mentioned in I no longer holds good, the oxysalts showing a greater conducting power than the haloid salts. This difference increases with increasing concentration, and with increasing electromotive force.

A clearer conception of the relations which hold is obtained by expressing the conducting power in terms of molecular conductivities. It is impossible to give absolute molecular conductivities, as this would require an exact knowledge of the concentration of salt vapour between the electrodes and of the capacity of the electrode system. In the following table the numbers, which are proportional to the molecular conductivities, have been obtained by dividing the numbers of the preceding table by the concentration of the solution, taking $\frac{1}{10}$ normal solutions as of unit concentration.

The values all refer to an E.M.F. of ·227 volt. At this E.M.F. Ohm's law is obeyed with close approximation in our experiments, so that the conditions correspond in this respect with those of conduction in aqueous solution, from which the idea of molecular conductivity is drawn.

Concentration of solution.	KCl.	KBr.	KClO ₃ .	KI.	KNO ₃ .	$\frac{N}{2}$ K ₂ SO ₄ .	$\frac{N}{2}$ K ₂ CO ₃ .	KOH.
·2	3·67	3·66	3·31	6·4	10·8	13·3
·1	5·75	5·74	...	6·2	9·35	11·0	11·2	...
·05	8·0	8·26	7·62	9·2	10·2	11·42	10·86	10·8
·02	14·8	15·7
·01	21·7	22·3	23·1	19·7	24·7	23·0	22·0	18·6
·002	...	75·0	...	67·0	72·5	...

Concentration of solution.	NaF.	NaCl.	NaBr.	NaI.	NaNO ₃ .	$\frac{N}{2}$ Na ₂ SO ₄ .	$\frac{N}{2}$ Na ₂ CO ₃ .	NaOH.
·5	·40	·41	·42	·44	...	·50	·49	·52
·2	·69	·71	·72	·70	·92	·80	·85	...
·1	...	1·15	1·30	...	1·30	...
·05	1·96	2·10	1·92	1·94	1·96

Concentration of solution.	LiCl.	LiNO ₃ .	RbCl.	RbNO ₃ .	CsCl.	CsNO ₃ .	HCl.
·5	·11	·18	·07
·1	·41	·53	11·3	25·9	22·2	36·6	...
·02	23·5	25·7	29·5	31·0	...
·004	60·2	56·3	75·5	74·2	...

The following conclusions may be drawn from the above tables:—

- I. In general, the molecular conductivity of a salt increases with increasing dilution.
- II. The oxysalts of all alkali metals behave differently to the haloid salts.*
- III. At all concentrations investigated, the conducting power of the oxysalts of any one metal is approximately the same.

With regard to the halogen salts, it appears that potassium iodide occupies an intermediate position, forming a transition member from the haloids to the oxysalts. Sodium bromide and iodide would appear to occupy a similar position among the sodium salts.

It appears also that with increasing concentration the molecular conductivity of the oxysalts attains a minimum value. This is very evident with the oxysalts of potassium, and recognisable in those of rubidium and caesium, the minimum values being 11, 26, and 34 in the respective cases.

* Potassium chlorate, being converted by the flame into the chloride, is an exception to this statement.

No minimum is observable in the case of the sodium or lithium salts, nor in the case of the chlorides of caesium, rubidium, and potassium, and the bromide of potassium. It is probable, however, that in the case of these salts a minimum value of the molecular conductivity would be found, if higher concentrations could be investigated, for this is distinctly observable in the case of potassium iodide. It will also be seen that with the oxysalts of potassium the minimum is only attained at higher concentrations than in the case of the oxysalts of rubidium and caesium.

The intermediate character of iodide of potassium is once more evident, for the minimum value of the molecular conductivity is about 6, whilst that for the bromide and chloride must be considerably less, and that for the oxysalts is 11.

In the case of the haloid salts the variation of conducting power with concentration may be approximately expressed by the equation

$$c = k \sqrt{q},$$

when c is conductivity, q the concentration, and k a constant.

This is shown for NaCl and KCl in the following tables:—

KCl.					NaCl.				
Concentration of solution.	E.M.F. 5.6 volts.		E.M.F. .227 volt.		Concentration of solution.	E.M.F. 5.6 volts.		E.M.F. .227 volt.	
	Found.	Calculated.	Found.	Calculated.		Found.	Calculated.	Found.	Calculated.
.2	31.9	(31.9)	7.34	(7.34)	.5	7.66	(7.66)	2.07	(2.07)
.1	21.0	22.6	5.75	5.20	.2	4.54	4.84	1.42	1.31
.05	14.1	15.9	4.00	3.67	.1	3.49	3.42	1.15	.93
.02	8.93	10.1	2.97	2.32	.05	2.95	2.42	1.05	
.01	6.02	7.1	2.17	1.65					
.005	5.47	5.0							
.002	4.03	3.2							

The agreement which here is by no means complete cannot be recognised at all in the oxysalts except at low concentrations. In this respect our results differ from those of ARRHENIUS, who gives the relation $c = k \sqrt{q}$ as one of general applicability. The chief cause of the difference in our results lies doubtless in the fact already mentioned, that, with a solution of given concentration, much more salt was carried into the flame in our experiments than in those of ARRHENIUS.

It is of interest to determine the variation of conducting power from metal to metal of the series of salts investigated. This is most satisfactorily done by making use of concentrations at which the individualities of the several salts of one metal have disappeared. On account of the relatively bad conducting power of the lithium and

sodium salts, experiments at great dilutions were not attempted with them. The greatest dilution at which all salts were examined was $\frac{1}{10}$ normal, and, although at this concentration the various salts of each metal do not conduct equally well, we may take the chloride as representing the haloid salts and the nitrate as representing the oxysalts. The following table gives the comparison:—

	Chlorides.			Nitrates.		
E.M.F.	5·60	·795	·227	5·60	·795	·227
Cæsium	123	60·5	22·2	303	115	36·6
Rubidium	41·4	26·4	11·3	213	82·4	25·9
Potassium	21·0	13·4	5·75	68·4	29·3	9·35
Sodium	3·49	2·45	1·15	3·88	2·67	1·32
Lithium	1·29	·87	·41	1·47	·99	·53
Hydrogen	·75	...	·27			

It is evident that the conductivity increases with increasing atomic weight of the metal, and that the increase is more rapid in the case of the oxysalts than in that of the haloids.

Influence of Temperature on Conductivity.

In the form of apparatus used by us a column of hot gases ascends from the lower cone of combustion to the upper one, the temperature rapidly decreasing. By altering the relative position of the electrodes and the mouth of the flame tube the electrodes could be brought into regions of different temperature. We do not attempt in the present enquiry to deal fully with the relation between the temperature of salt vapours and their conductivity, but have contented ourselves with making a few experiments, so as to gain an idea of the general order of the relationship.

By means of two millimetre scales etched on opposite sides of the glass cylinder, G (fig. 3), the distance between the tip of the inner cone and the lower edge of the electrodes (which in these experiments were square plates of platinum) was adjusted to 5, 15, and 25 millims. in the respective cases.

To measure the temperature, a platinum platinum-rhodium thermo-couple was placed first 2 millims. above, then 2 millims. below the electrodes in the axis of the flame, and the mean of the galvanometer readings taken to represent the temperature of the vapour between the electrodes. The solution sprayed in all cases was $\frac{1}{4}$ normal sodium carbonate.

The following table contains the results; the observations were repeated in the order given, so as to control their accuracy:—

	Height of lower edge of electrodes above tip of inner cone.	Position of thermo-couple.	Temperature deflection.	Conductivity.
(1)	5 millims.	2 millims. above	256	235
	5 "	2 " below	375	215
(2)	25 "	2 " above	237	85
	25 "	2 " below	311.5	80
(3)	15 "	2 " above	250	135
	15 "	2 " below	334	125
(4)	25 "	2 " above	240	86
	25 "	2 " below	314	80
(5)	5 "	2 " above	259	235
	5 "	2 " below	376	215

It will be seen from the above table that the temperature registered by the thermo-couple, when below the electrodes, is much higher than when above. The numbers representing the conducting power are otherwise, a slightly lower reading being obtained when the thermo-couple was below the electrodes. This is, of course, due to the cooling effect of the thermo-couple, which in the lower position was immersed in the gases before they reached the electrodes.

It should be stated that the cylindrical column of interconal gases and salt vapour was not appreciably altered by changes in position of the flame tube, so that the quantity of salt vapour between the electrodes was sensibly the same in all cases.

The end result of the above experiments may be expressed as follows :—

Temperature of vapour.	Conducting power.
316.5	225
292	130
275.6	82.7

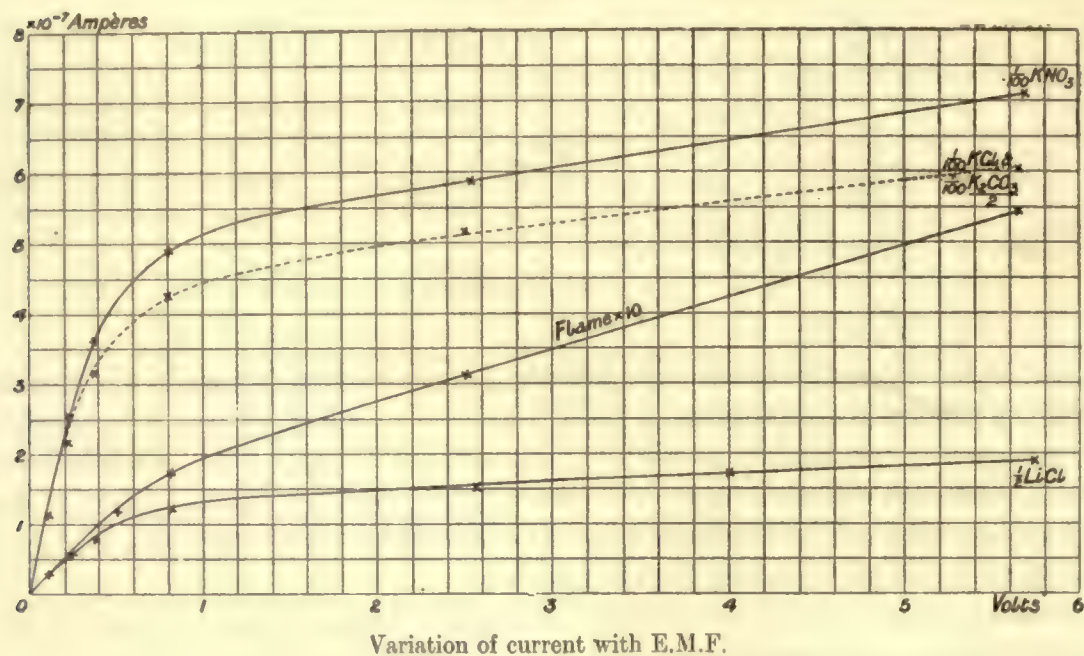
These readings are on an arbitrary scale, but they show very clearly that the conducting power increases rapidly with increasing temperature, and that at temperatures not greatly below those which the vapour attains in flames the conductivity would become inappreciable. It may be stated that the temperature intervals in the above table correspond approximately to 140 and 95 Centigrade degrees.

Relation between Current Strength and Electromotive Force.

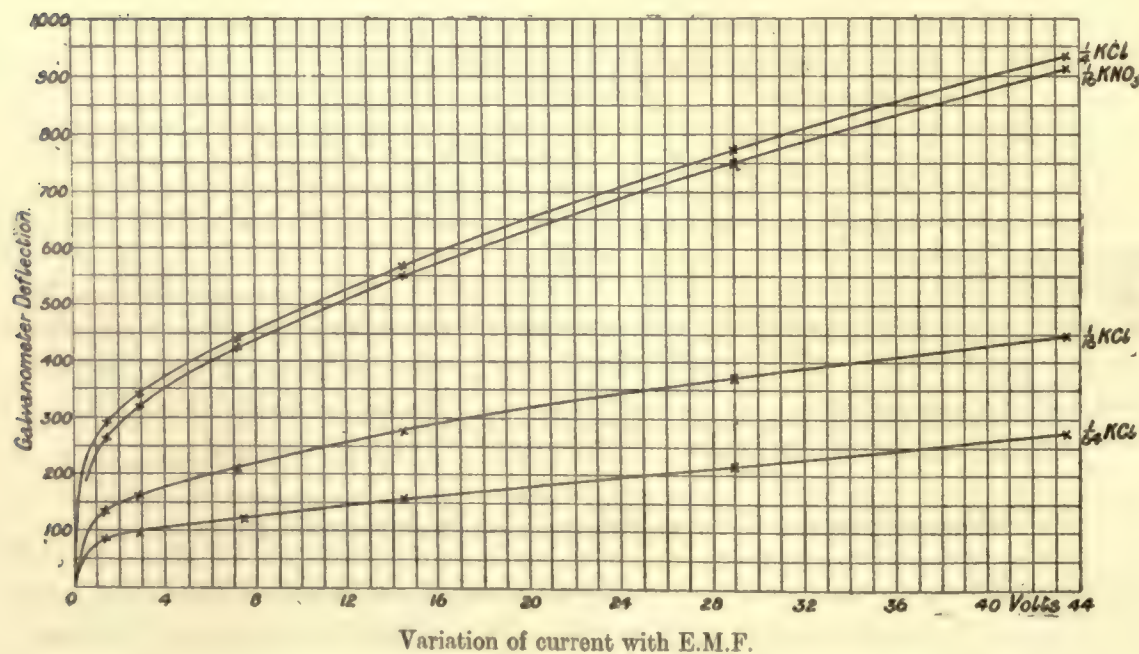
Experiments on the relation between current strength and electromotive force were carried out with a large number of salts, and with a difference of potential between

the electrodes, which varied from .01 volt to 45 volts. The results show that with small electromotive forces up to .2 volt, Ohm's law is accurately obeyed. With greater electromotive forces the law is not obeyed, and the deviations increase with increasing electromotive force. The results are plotted on the Curves V to IX.

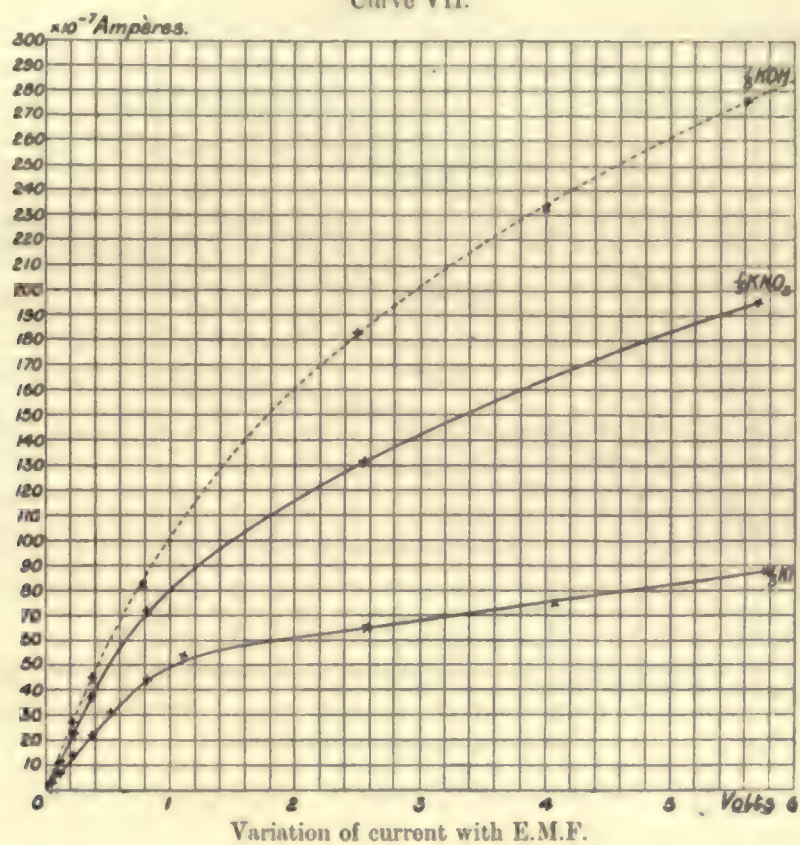
Curve V.



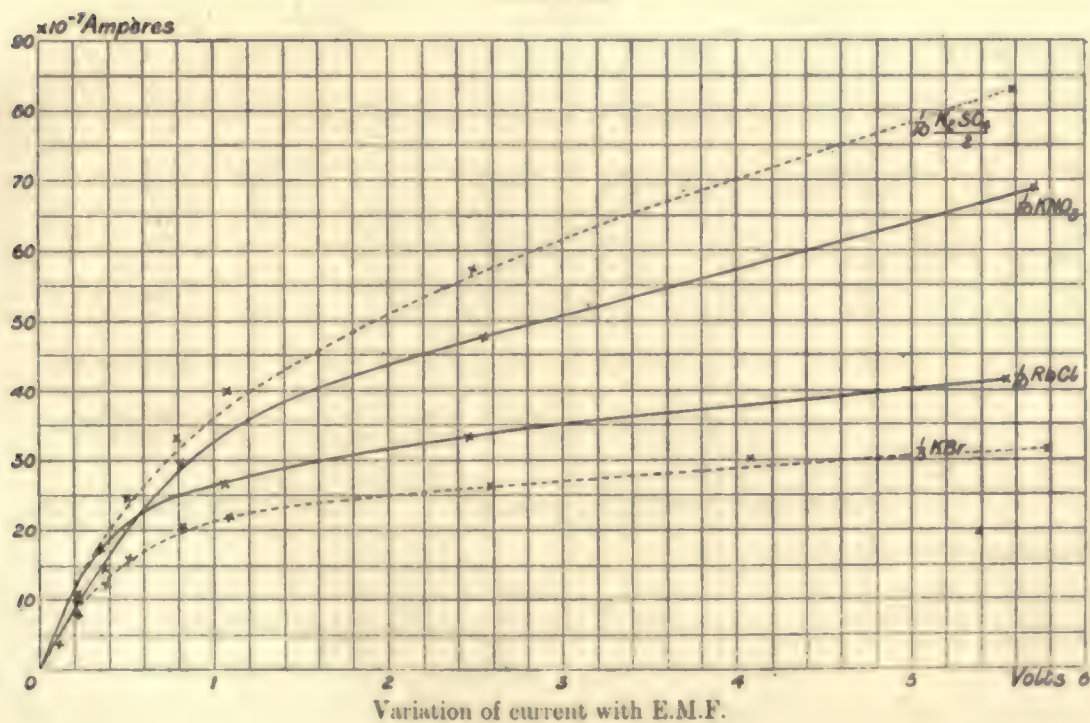
Curve VI.



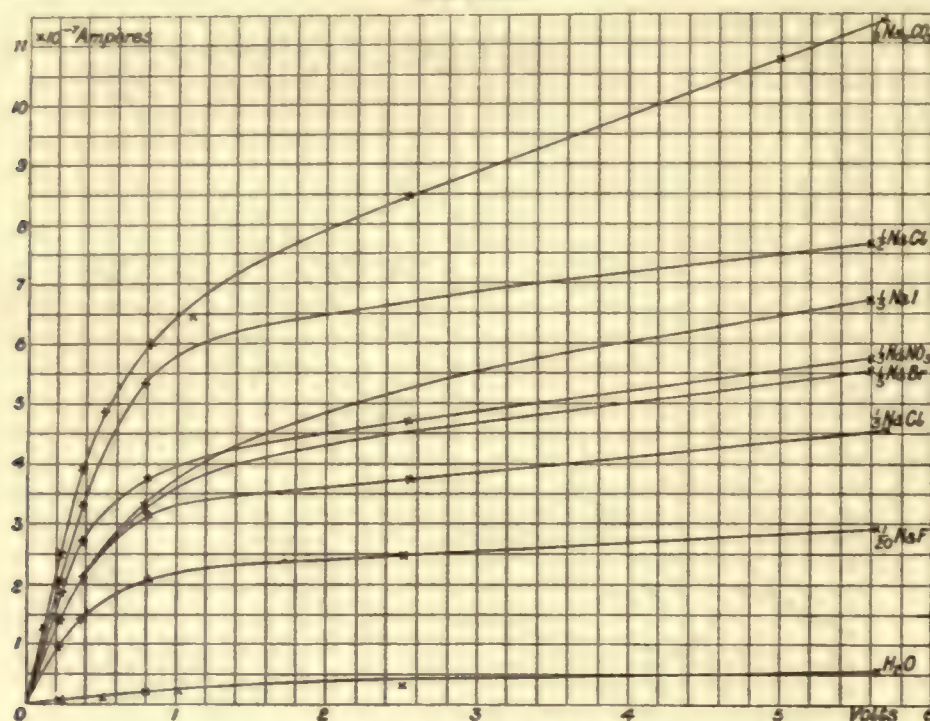
Curve VII.



Curve VIII.



Curve IX.



Variation of current with E.M.F.

The following two tables sufficiently indicate the degree to which Ohm's law is obeyed by vaporised salts:—

E.M.F.	Ratio.	$\frac{N}{64}$ KBr.		$\frac{N}{64}$ K_2SO_4 .		$\frac{N}{16}$ KCl.		$\frac{N}{16}$ KBr.	
		Deflection.	Ratio.	Deflection.	Ratio.	Deflection.	Ratio.	Deflection.	Ratio.
volt.									
.1	10	30.2	9.90	27.3	9.92	53.1	10.03	50.7	10.15
.08	8	23.9	7.84	21.0	8.00	42.1	7.94	40.6	8.12
.06	6	18.2	5.97	16.65	6.06	32.0	6.04	30.6	6.10
.04	4	12.0	3.93	10.95	3.98	21.05	3.96	20.25	4.05
.02	2	6.1	2.00	5.45	1.98	10.65	2.01	10.15	2.03
.01	1	3.05	1.00	2.75	1.00	5.3	1.00	5.0	1.00

E.M.F.	Ratio.	$\frac{N}{64}$ KI.		$\frac{N}{4}$ KCl.		$\frac{N}{16}$ KNO_3 .	
		Deflection.	Ratio.	Deflection.	Ratio.	Deflection.	Ratio.
volt.							
44.5	3708	305	85.9	935	118	611	129
1.5	126	87.2	24.5	290	36.7	188	39.6
.12	10	24.7	9.77	78.5	9.94	47.5	10
.012	1	3.55	1	7.9	1	4.75	1

Our results are in harmony with those of ARRHENIUS in so far as they show that Ohm's law is only valid at low electromotive forces in the case of vaporised salts.

To express the general relationship between current strength and electromotive force, ARRHENIUS gives the equation $C = Af(E)$, where C = current strength, E = electromotive force, and A = a constant dependent on the solution sprayed. He found that for any electromotive force (E), $f(E)$ was the same for solutions of different salts and of different concentrations.

The validity of this equation is also confirmed by our observations up to a certain point, but with more concentrated solutions marked divergence is apparent. This will be evident from the following table.

The $\frac{1}{100}$ normal solutions of potassium salts which we investigated all gave approximately the same current for any one electromotive force. We have, therefore, used these to calculate some values of $f(E)$. Taking $f(E) = 1$ when $E = 5$ volts, we get from the numbers for $\frac{1}{100}$ normal KCl and $\frac{1}{100}$ normal K_2CO_3 solutions the following values:—

E.	$f(E)$.
volts.	
2	·850
1	·760
·7	·709
·5	·638
·2	·332

From these values of $f(E)$ we calculate the current which should be found in the case of a series of salts, and the numbers so obtained are inserted in a table side by side with those indicating the currents actually measured:—

E.M.F.	$\frac{N}{100} KNO_3$		$\frac{N}{5} KOH$		$\frac{N}{5} KBr$		$\frac{N}{2} Na_2CO_3$		$\frac{N}{5} NaCl$	
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.
2	5·64	5·80	15·8	22·2	2·47	2·62	7·86	9·12	3·62	3·73
1	5·07	5·18	9·85	19·8	2·16	2·34	6·38	8·16	3·28	3·33
·7	4·70	4·84	7·60	18·5	1·90	2·18	5·65	7·61	3·00	3·11
·5	4·22	4·35	3·60	16·6	1·53	1·96	4·73	6·84	2·63	2·80
·2	2·25	2·26	2·31	8·65	·64	1·02	2·30	3·56	1·30	1·46

It is evident from the foregoing table that the formula $C = Af(E)$ does not express the relation existing between current strength and electromotive force over the series of observations made by us.

We are indebted to Professor J. J. THOMSON for a suggestion which has led us to

an equation capable of expressing the relationship in question in a remarkably complete way. In a paper published by Professor THOMSON and Mr. RUTHERFORD in the 'Phil. Mag.' ((V.) vol. 42, p. 392 (1896)), an account is given of the passage of electricity through gases exposed to Röntgen rays. According to the authors, the current through a gas exposed to Röntgen radiation between two parallel plates increases more and more slowly as the potential difference between the plates is increased, until finally a maximum current is obtained which remains constant under all further increase of potential difference. The electromotive force corresponding to the attainment of this state is called a saturating E.M.F. Assuming that the conductivity of Röntgenised gas is due to the presence of free ions, and that the rate of disappearance of these ions by recombination to form neutral molecules is proportional to the square of the concentration of the ions, THOMSON and RUTHERFORD give the following formula, $I - i = A \frac{i^2}{E^2}$, where I is the maximum current for a saturating E.M.F., i is the current strength for any electromotive force E , and A a constant.

Röntgenised gases and the gases of a flame exhibit a noteworthy similarity in their behaviour. Thus both rapidly lose their power of conducting electricity when they pass from the source where they have acquired this power. Both also lose their conductivity when passed between a pair of electrodes maintained at different potentials. (GIESE, 'Wied. Ann.,' vol. 17, p. 517, 1882.) That the conductivity in both cases may be due to ions has been suggested by previous investigators.

A glance at the curves in which THOMSON and RUTHERFORD plot the relation between current strength and electromotive force, will show that there is a general resemblance to the Curves I to V, by which our own results are plotted. The current through the flame, however, continues to increase even when a large E.M.F. is applied, whilst that through a Röntgenised gas reaches an almost constant value.

For potentials above one volt our curves are almost rectilinear, so that the relationship between current and E.M.F. may, for E.M.F.s above 1 volt, be expressed by the equation

$$c = I + k_1 E \quad \dots \quad (1)$$

that is to say, the current strength may be represented as composed of two parts, one being a constant quantity and the other a quantity proportional to the E.M.F. This equation, however, does not give us the value of the current for small E.M.F.s.

If we represent the relation between the current and E.M.F. at all E.M.F.s by the equation

$$c = i + k_1 E,$$

then i is a variable which at high E.M.F. attains a constant value I exactly as the current through a Röntgenised gas attains a constant value.

From the analogy of the flame conductivity to that of Röntgenised gases, we

assume that the equation used by THOMSON and RUTHERFORD to represent the relation between the current and the E.M.F. in their experiments should also represent the relation between i and the E.M.F. in our experiments.

Accordingly, then, the equations

$$c = i + k_1 E \quad (2)$$

$$I - i = k_2 \frac{i^2}{E^2} \quad (3)$$

should represent the value of the current strength at all E.M.F.s in our experiments. In the case of Röntgenised gases $k_1 = 0$, or is very small, so that $c = i$.

In the following tables the observed currents for various salts are compared with those calculated by means of equations (2) and (3), and curves calculated by means of these equations, using in each case the values given below for k_1 , k_2 and I , are dotted in the curve diagrams V, VII, and VIII. The points marked near them show the experimentally determined currents.

$$\frac{N}{100} \text{ KCl and } \frac{N}{2} \text{ K}_2\text{CO}_3. \quad \begin{aligned} I &= 4.50 \times 10^{-7}. \\ k_1 &= .278 \times 10^{-7}. \\ k_2 &= .020 \times 10^{-7}. \end{aligned}$$

E.M.F.	Current (calculated).	Current (from curve in Diagram IV).
volts.	amperes.	amperes.
.076	1.02×10^{-7}	$.80 \times 10^{-7}$
.179	2.05 "	1.83 "
.346	3.10 "	3.10 "
.80	4.22 "	4.30 "
1.09	4.50 "	4.53 "
2.00	4.96 "	5.00 "
5.00	5.87 "	5.90 "

$$\frac{N}{10} \frac{\text{K}_2\text{SO}_4}{2}. \quad \begin{aligned} I &= 4.23 \times 10^{-6}. \\ k_1 &= .74 \times 10^{-6}. \\ k_2 &= .148 \times 10^{-6}. \end{aligned}$$

E.M.F.	Current (calculated).	Current (from experimental curve).
volts.	amperes.	amperes.
.10	$.574 \times 10^{-6}$	$.55 \times 10^{-6}$
.214	1.16 "	1.12 "
.516	2.38 "	2.50 "
1.04	3.77 "	3.90 "
3.20	6.36 "	6.40 "
5.00	7.83 "	7.87 "

$\frac{N}{5}$ KOH.

$I = 16.9 \times 10^{-3}.$

$k_1 = 2.10 \times 10^{-6}.$

$k_2 = .141 \times 10^{+3}.$

E.M.F.	Current (calculated).	Current (from experimental curve).
volts.	amperes.	amperes.
.085	1.07×10^{-6}	$.96 \times 10^{-6}$
.184	2.28 "	2.13 "
.407	4.75 "	4.80 "
.666	7.30 "	7.30 "
1.18	11.3 "	11.1 "
2.00	16.1 "	15.8 "
4.08	23.6 "	23.6 "
5.97	28.4 "	28.2 "

 $\frac{N}{5}$ KBr.

$I = 2.41 \times 10^{-6}.$

$k_1 = .135 \times 10^{-6}.$

$k_2 = .158 \times 10^{+6}.$

E.M.F.	Current (calculated).	Current (from experimental curve).
volts.	amperes.	amperes.
.213	$.73 \times 10^{-6}$	$.70 \times 10^{-6}$
.335	1.05 "	1.07 "
.625	1.59 "	1.73 "
.802	1.81 "	2.00 "
1.25	2.17 "	2.23 "
1.91	2.46 "	2.45 "
2.76	2.67 "	2.69 "
3.50	2.81 "	2.85 "
4.50	3.00 "	3.02 "
6.00	3.21 "	3.20 "

 $\frac{N}{5}$ NaCl.

$I = 3.10 \times 10^{-7}.$

$k_1 = .258 \times 10^{-7}.$

$k_2 = .030 \times 10^{+7}.$

E.M.F.	Current (calculated).	Current (from experimental curve).
volts.	amperes.	amperes.
.12	1.03×10^{-7}	$.80 \times 10^{-7}$
.33	2.08 "	2.00 "
.40	2.30 "	2.30 "
.74	2.89 "	3.05 "
1.12	3.19 "	3.30 "
2.00	3.55 "	3.60 "
3.00	3.85 "	3.88 "
5.00	4.39 "	4.40 "

The agreement of the calculated and observed values in the above tables shows that the relation between the current and E.M.F. in our experiments can be represented with considerable accuracy by the formula in question.

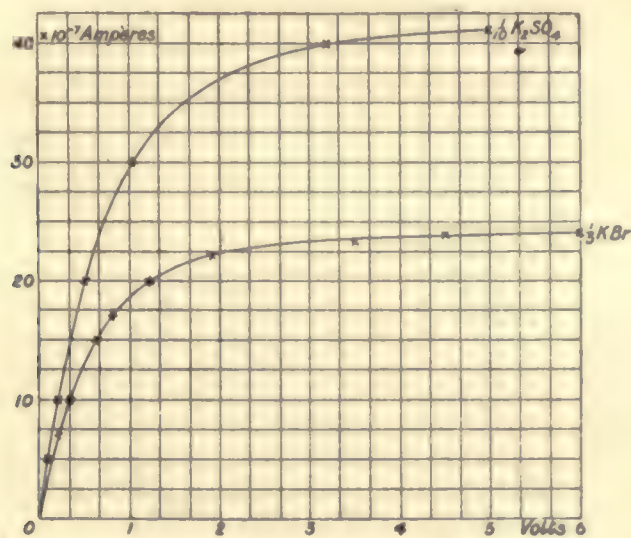
In order to show that i gradually attains a maximum value in our experiments as the E.M.F. is increased, the calculated values of i are inserted in a separate column of the foregoing tables.

In the case of $\frac{1}{100}$ normal KCl, $\frac{1}{100}$ normal K_2CO_3 , $\frac{1}{10}$ normal K_2SO_4 , and $\frac{1}{5}$ NaCl, it will be seen that i has almost reached its maximum value, that is, it has become nearly equal to I at an E.M.F. of 5 volts.

In the case of $\frac{1}{5}$ KBr, this is the case at 6 volts, whilst in the case of $\frac{1}{5}$ KOH the maximum value is not quite reached at 6 volts.

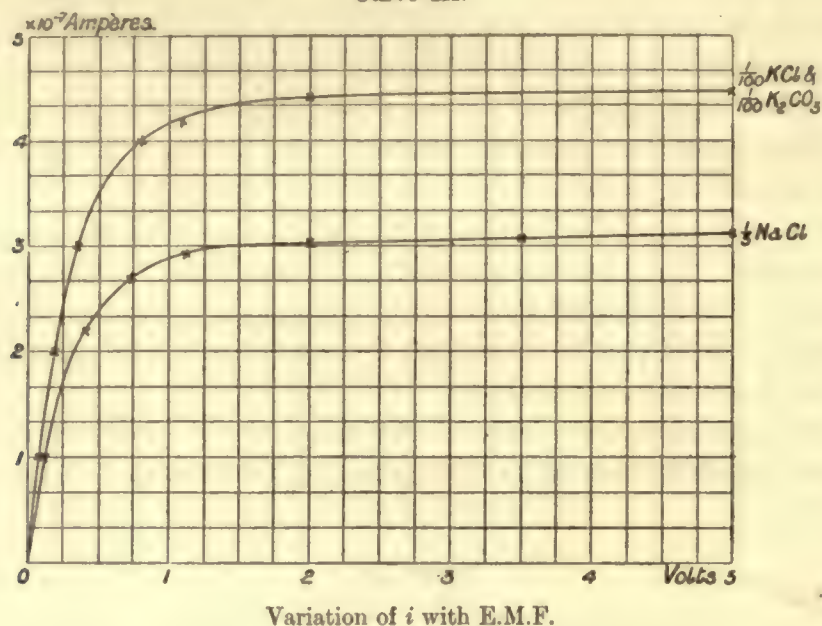
The values of i are plotted in Curves X and XI. As was to be expected, the form of these curves is perfectly similar to those given by THOMSON and RUTHERFORD.

Curve X.



Variation of i with E.M.F.

Curve XI.



We will conclude this section by showing what relation must hold between the constants I , k_1 , and k_2 , in order that the equation used by ARRHENIUS (see *ante*, p. 113), $C = Af(E)$, where $f(E)$ has the same value for all solutions, may hold good.

Solving $I - i = k_2 \frac{i^2}{E^2}$ for i , we get

$$i = -\frac{E^2}{2k_2} \pm \frac{E}{2} \sqrt{\frac{E^2}{2k_2^2} + \frac{4I}{k_2}}.$$

Now $C = i + k_1 E$.

Substituting the above value for i , we have

$$\begin{aligned} C &= E \left\{ k_1 - \frac{(E - \sqrt{4Ik_2 + E^2})}{2k_2} \right\} \\ &= IE \left\{ \frac{k_1}{I} - \frac{(E - \sqrt{4Ik_2 + E^2})}{2Ik_2} \right\}. \end{aligned}$$

From this it follows that if Ik_2 and $\frac{k_1}{I}$ have the same values for all solutions, then $f(E)$ in the equation of ARRHENIUS, $C = Af(E)$, will be of the same form for all solutions.

According to THOMSON and RUTHERFORD (*loc. cit.*), k_2 should be a constant for any one substance, whatever the concentration.

The following table contains some values of the quantities I , k_1 , k_2 , $\frac{k_1}{I}$, and Ik_2 for various solutions :—

Solution.*	$I \times 10^{-7}$.	$k_1 \times 10^{-7}$.	$k_2 \times 10^{-7}$.	$\frac{k_1}{I}$.	Ik_2 .
$\frac{1}{3}$ KOH	169	21	·0141	·124	2·38
$\frac{1}{3}$ KI	46·0	7·1	·0140	·154	·645
$\frac{1}{10}$ K_2SO_4	42·3	7·4	·0148	·175	·626
$\frac{1}{2}$ KBr	24·1	1·35	·0158	·056	·381
$\frac{1}{20}$ K_2CO_3	14·5	2·4	·0143	·166	·207
$\frac{1}{30}$ KNO_3	6·66	·713	·0144	·107	·096
$\frac{1}{30}$ KCl	6·38	·55	·0144	·086	·092
$\frac{1}{100}$ KNO_3	4·83	·395	·0154	·082	·075
$\frac{1}{100}$ KCl	4·50	·278	·0200	·062	·090
$\frac{1}{2}$ Na_2CO_3	6·11	·927	·0301	·152	·184
$\frac{1}{2}$ NaCl	5·5	·383	·0296	·0696	·163
$\frac{1}{3}$ NaCl	3·1	·258	·0300	·083	·093
$\frac{1}{20}$ NaF	2·12	·147	·044	·0694	·093
$\frac{1}{10}$ $RbNO_3$	120	18·6	·00910	·155	1·09
$\frac{1}{10}$ RbCl	25·2	2·56	·00915	·102	·23
$\frac{1}{30}$ RbCl	10·8	1·04	·0124	·104	·134
$\frac{1}{230}$ RbCl	4·70	·412	·0228	·088	·107
$\frac{1}{10}$ $CsNO_3$	148	27·8	·0066	·188	·976
$\frac{1}{10}$ CsCl	53·5	6·43	·00682	·120	·365
$\frac{1}{30}$ CsCl	12·0	1·09	·0072	·091	·087
$\frac{1}{230}$ CsCl	5·91	·465	·0122	·0786	·072
$\frac{1}{2}$ LiCl	1·24	·114	·083	·092	·102
$\frac{1}{10}$ LiCl	·83	·0825	·128	·099	·106

It is clear from the above numbers that $\frac{k_1}{I}$ varies considerably, according to the solution sprayed. Nevertheless, the values for the more dilute solutions do not differ much from ·08.

k_2 has nearly equal values for the salts of each metal, except for values of I less than about 5×10^{-7} ampere. Below this, k_2 increases as I diminishes, so that Ik_2 is nearly constant.

We have thus the following values of $k_2 \times 10^{-7}$ when I is greater than 5×10^{-7} .

* The concentration is given in terms of a normal solution.

Cæsium Salts	. . .	·0066
Rubidium „	. . .	·0091
Potassium „	. . .	·0144
Sodium „	. . .	·0300
Lithium „	. . .	·08

When I is below 5×10^{-7} , then Ik_2 has nearly the same value for all solutions, viz., $Ik_2 = \cdot 09$.

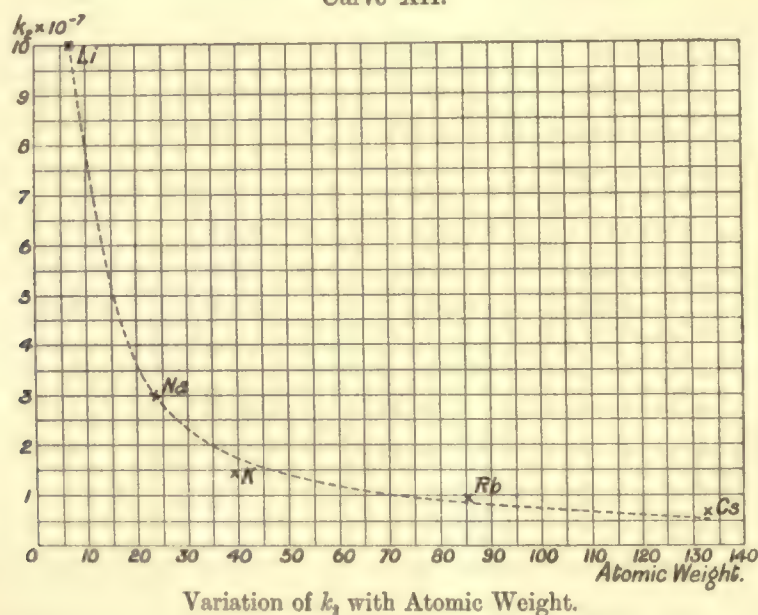
It thus appears that both $\frac{k_1}{I}$ and Ik_2 are nearly of the same value for all solutions, provided I is less than 5×10^{-7} , so that for dilute solutions ARRHENIUS'S equation $C = Af(E)$ holds good. When, however, I is greater than this, k_2 becomes constant, so that Ik_2 increases proportionally to I , and $f(E)$ changes in form.

This increase in Ik_2 corresponds to a decrease in the slope of the beginning of the curves, so that as the concentration of the solution is increased, the curves bend over more and more gradually towards the axis of E.M.F.

In Curve XII the variation of k_2 with the atomic weight of the metal is shown.

The points fall nearly on the curve, $Mk_2 = \cdot 7$ ($M = \text{Atomic Weight}$) which is drawn.

Curve XII.



Conductivity of Flames containing Acids.

Since the majority of acids are decomposed at the temperatures employed in our experiments, our investigation of the effect of acids on the conductivity of the flame was limited to hydrochloric and sulphuric acids.

It has already been shown that the free flame has a measurable though small conductivity, and, for the sake of comparison, the numbers obtained on p. 98 are appended to those obtained by spraying half normal solutions of HCl and H_2SO_4 .

E.M.F.	Distilled water.	$\frac{N}{2}$ HCl .	$\frac{N}{2}$ H_2SO_4 .
5.60 .227	.54 .055	1.46 .396	.510 .105

The conductivity of the acids is thus very small in comparison with that of the alkali salts.*

We also investigated the conductivity of ammonium chloride, and found it to be almost the same as that of an equivalent solution of hydrochloric acid. This is readily explained by the dissociation of the salt into HCl and NH_3 at the temperature of the experiment.

The following values, corrected for the conductivity of the free flame, were obtained :—

E.M.F.	$\frac{N}{2}$ NH_4Cl .	$\frac{N}{2}$ HCl .	$\frac{N}{2}$ H_2SO_4 .
volts. 5.6 .227	1.03 .321	.92 .341	— .03 .05

In the flame the H_2SO_4 is no doubt largely decomposed, yielding sulphur dioxide, whilst the hydrochloric acid is more stable. This accounts for the greater conductivity of the hydrochloric acid.

It is possible that in these cases, where the conductivity is small, dust particles entering with the air may have an appreciable effect. It is impossible to estimate this effect; we sought to reduce it as far as possible by filtering the air through cotton wool. If we consider it to have been insignificant, it is possible to make a comparison of the conducting power of water and hydrochloric acid in the flame. The quantity of water vapour in the flame with a spray of distilled water was many hundred times, probably many thousand times, the quantity of hydrochloric acid in the flame when a half normal solution was sprayed. The numbers given above show that the conductivity of the hydrochloric acid is at least two or three times that due to the water vapour alone.

Experiments with Decolorized Flames containing Salt Vapours.

The introduction of chloroform vapour into a flame coloured by the vapour of a lithium salt completely destroys the coloration (SMITHELLS, 'Phil. Mag.' (V), 39, 122, 1895). The chloroform affords a convenient means of supplying an abundance of

hydrochloric acid along with combustible carbon, and the first action in the flame may be expressed by the equation :



Experiments were made with flames containing chloroform vapour together with salt spray, in order to discover if any relation existed between the conditions requisite for coloration and those which determine conductivity.

In order to introduce the chloroform at any moment into the flame without disturbance of the experimental conditions, the apparatus was so arranged that by means of a three-way tap the gas supply could be passed through one or other of two similar U-tubes placed "in parallel," one containing a little water and the other an equal volume of chloroform. The flame remained steady when the change was made from one course to the other, and by use of a thermo-couple we found that the temperature in the neighbourhood of the electrodes likewise was not sensibly affected.

The following table gives a comparison of the conductivity of the flame containing lithium salts in the coloured and colourless states :—

	$\frac{\text{N}}{2}$ LiCl.		$\frac{\text{N}}{10}$ LiNO ₃ .	
E.M.F.	5·60	·227	5·60	·227
Current strength :				
Coloured flame	2·14	·547	2·01	5·87
Colourless „	2·44	·251	4·50	5·39

The above figures show that the conducting power is not destroyed when the flame is decolorized. It appears that the influence of the introduction of chloroform on the conductivity, such as it is, varies with the E.M.F. employed. At 5·6 the conductivity is uniformly increased when chloroform is added, whilst at ·227 volt a diminution is observed in both cases.

If the conductivity of the flame alone (that is, without salt) and of the flame with chloroform alone be subtracted from the above numbers, we obtain the following values for the salt alone :—

	5·6 volts.	·227 volt.
$\frac{\text{N}}{2}$ LiCl :		
Coloured flame . . .	1·7	·50
Decolorized flame . .	1·5	·17
$\frac{\text{N}}{10}$ LiNO ₃ :		
Coloured flame . . .	1·5	·52
Decolorized flame . .	3·0	·41

As the lithium salts have but a small conductivity in the flame, it was thought possible that the alteration of conductivity above tabulated might depend on the large excess of hydrochloric acid in the flame. The experiments were therefore extended to the salts of caesium and potassium, which have so high a conductivity as to preclude the possibility just suggested.

In the following table the results are given in scale deflections :—

E.M.F. in volts . . .	5.60	1.08	.227	.028
CsCl solution :				
Coloured flame	850	740	264	33
Decolorized flame	1410	700	212	26
KCl solution :				
Coloured flame	55	...	105	
Decolorized flame	78	...	93	

The above figures show that just as in the case of lithium salts, the conductivity of flames containing the salts of caesium and potassium does not disappear on removal of the colour by means of chloroform, and the influence of the E.M.F. on the changes of conductivity that are noticed is the same in form as in the case of the lithium salts. It appears that at a certain E.M.F. the addition of chloroform would produce no effect in the conductivity. For the caesium chloride solution used it follows from the table that this E.M.F. would be about 1.1 volt.

Conductivity of Salts vaporised in the Flame of Cyanogen.

It has already been stated in the introduction that the equal conductivity of various salts of the same metal was attributed by ARRHENIUS to the conversion of each salt into hydrate by the large excess of water vapour present.

It appeared of interest to investigate the behaviour of salts in a gaseous medium containing only a small percentage of water vapour, and for this purpose we chose the flame of cyanogen. To avoid the presence of water altogether is impracticable, if the salt has to be sprayed; but if we suppose that in a coal-gas flame any considerable proportion of the hydrogen has been burned before it reached the neighbourhood of the electrodes, the quantity of water vapour in such a flame will be very great compared with that of a cyanogen flame, in which the only water is that introduced by the sprayer (partly as drops and partly as water vapour). As we estimated this difference in the amount of water to be something like 10 to 1, we thought it probable that, if the hypothesis of ARRHENIUS were correct, marked

differences of conductivity should be observable when salts in suitably concentrated solution were sprayed in the flames of coal-gas and cyanogen. For this purpose $\frac{1}{50}$ normal solutions of potassium salts were employed. In a coal-gas flame solutions of this concentration conduct equally well, but in a cyanogen flame, where no water is produced by combustion, such solutions should act like the more concentrated solutions in a coal-gas flame, that is to say, their individual conductivities should become apparent.

In carrying out the experiments the limited amount of cyanogen available* at one time necessitated some alterations in the apparatus. The vessels for the collection of coarse spray were removed, and the flame tube connected directly to the tubulated cylinder, into which the sprayer projected. The flame was not separated into its two cones, and just enough air used to keep the sprayer steadily in action. The amount of salt entering the flame was not greatly different from what it was with the apparatus in its ordinary form.

The following results were obtained with an E.M.F. of 5.55 volts :—

Experiment No. 1.		Experiment No. 2.	
Solution.	Conductivity.	Solution.	Conductivity.
$\frac{N}{50}$ KCl	167.0	$\frac{N}{50}$ KBr	199.0
$\frac{N}{50}$ K ₂ SO ₄	177.0	$\frac{N}{50}$ KNO ₃	205.0
Distilled water	6.4	Distilled water	5.7

After each of the above experiments a measurement was carried out with a coal-gas flame under exactly the same conditions of pressure. This gave the following numbers :—

Experiment No. 1.		Experiment No. 2.	
Solution.	Conductivity.	Solution.	Conductivity.
$\frac{N}{50}$ K ₂ SO ₄	19.4	$\frac{N}{50}$ KBr	21.8

Subtracting the conductivity of the flame without salt, and correcting for a slight variation in the condition between the two cyanogen experiments, we have the following values :—

* One cubic foot stored over mercury in an iron gas-holder.

$\frac{N}{50}$ KCl.	161,
„ KBr	163,
„ KNO ₃	169,
„ K ₂ SO ₄	171.

The conductivities of the four salts are almost equal at the concentration used; the two haloid salts have somewhat less values than the two oxysalts.

It appears, therefore, that the smaller quantity of water in the cyanogen flame has not had a marked effect in bringing out the individual conductivities of the salts. It would, however, be unsafe to draw any positive conclusion as to the cause of conductivity from these experiments. We were deterred from prosecuting the enquiry further, because of the non-comparable character of the two flames in respect of temperature, a factor which has so great an influence on conductivity.

It will be noticed that the conductivity of salts in a cyanogen flame is about ten times that which they have in a coal-gas flame. The cyanogen flame without salt also conducted about ten times as well as the coal-gas flame without salt. We found that a cyanogen flame, into which a bead of salt was introduced by means of a platinum wire, showed a very high degree of conductivity. This was largely due to the very rapid rate at which the bead was vaporised; it shows at the same time that high conductivity may occur in the absence of hydroxides.

Consideration of Results.

We have not given, and do not think it necessary to give, an account of all previous investigations on the electrical conductivity of flame gases.* In recent times the conductivity of salt vapours has been investigated by WIEDEMANN and EBERT ('Wied. Ann.,' 35, 209, 1888), J. J. THOMSON ('Phil. Mag.,' (V), 29, 356 and 441), and by ARRHENIUS (*loc. cit.*), with a view to determining its character, whether electrolytic or otherwise. WIEDEMANN and EBERT, working with high electromotive force and comparatively cool electrodes, came to the conclusion that the discharge through flames was of a disruptive character, and facilitated in different degrees by the vapours of different salts. THOMSON, using a highly heated porcelain tube, provided with platinum electrodes, considered his results to indicate an electrolytic conduction. The conclusions of ARRHENIUS, as has already been stated, are entirely in favour of the view that the conduction of salt vapours is electrolytic in character.

Our own results do not seem to admit of any other explanation than that the conduction of salt vapours is electrolytic in character. At the same time the features presented by the conduction in the case of salt vapours do not correspond in every particular to those of the conduction of salts when dissolved in liquid solvents. In

* A good summary is given by HEMPTINNE ('Zeitschf. f. Phys. Chem.,' 12, 244, 1893).

the case of salt vapours, the high temperatures at which alone the conductivity can be examined, the correspondingly greater mobility of the molecules or ions, as well as the enormous reduction in the density and viscosity of the medium, and in the concentration of the salt, give ample ground for expecting characteristics in the phenomena of conduction very different from those which occur with liquid electrolytes at ordinary temperatures, although in both cases the conduction may be of a truly electrolytic character.

To take first of all the relation between current strength and electromotive force, we have in the case of liquid electrolytes, provided polarisation of the electrodes is avoided, a strict applicability of Ohm's law. In the case of salt vapours this law only applies for low electromotive forces. This was found both by ARRHENIUS and ourselves. ARRHENIUS, from theoretical considerations, believes that Ohm's law should hold also for higher electromotive forces, and he concludes that the divergence from it must be regarded as only apparent. This, however, leaves the divergence entirely unexplained.

For an expression capable of representing the relationship between current strength and electromotive force we were led, as already stated, to a formula derived by Professor J. J. THOMSON and Mr. RUTHERFORD from their study of the conductivity of gases subjected to Röntgen rays. In a gas exposed to Röntgen rays a steady supply of ions is supposed to be generated and the resulting concentration of ions is then determined by the fact that the rate at which they combine is proportional to the square of the number present, assuming equal numbers of positive and negative ions to be distributed throughout the gas. In a flame containing salt vapour it may be supposed that a steady supply of ionising salt is carried up between the electrodes, so that the conditions would be, to this extent, analogous in the two cases.

In applying the formula to our results we have had to recognise a feature distinguishing the behaviour of salt vapours from that of Röntgenised gases, namely, the fact that the current strength continues to rise slowly even at high E.M.F.s. The explanation of this difference does not seem to be difficult.* It would be accounted for by the increased electrostatic field either bringing in ions from the neighbourhood of the electrodes or increasing the rate of ionisation between them.

We have now to consider our results in reference to the question of the state in which the salts exist in the flame, and give rise to the conductivity. It could hardly be expected, *prima facie*, that the salts would all be vaporised without change, for even those among them that are most stable under ordinary conditions are likely to undergo some change of composition at the very high temperature reigning in the flame, and in the presence of various flame gases. The liability to change is indeed so great, and, at the same time, the precise character and extent of the change so little

* A kind of convective conduction, proportional to the E.M.F. which ARRHENIUS recognised in his experiments on alkaline earth metals, cannot here be in question. We have referred to this subject in another connection on p. 98.

known from independent evidence, that great caution is necessary before declaring that the results of such experiments as we have undertaken establish any one possible view.

The most important generalisations derivable from our study of the relation between current strength and concentration of different sets of salts of different metals are first, that the conductivities differ always according to the metal; secondly, that among salts of the same metal differences of conductivities evident at high concentrations disappear when the dilution is greater; and thirdly, that the conductivity of haloid salts is different from the conductivity of oxysalts.

We will give the explanation of these general facts, which appears to be most in conformity with our results, and most compatible with chemical evidence.

The fact that the conductivity of haloid salts at higher concentrations is approximately proportional to the square root of the concentration is consistent with the presence of a binary electrolyte, and as we have found that the conductivity of chlorides is maintained when the presence of a large quantity of chloroform in the flame forbids us to suppose that the chlorides are chemically altered, we conclude that the binary electrolyte in question is the haloid salt itself.

Again, the approximately equal conductivity of the oxysalts of any one metal which approaches that of the hydrates, indicates that in the flame they are changed into the same electrolysable substance, which we conclude is the hydroxide or oxide.

At the same time, whilst we recognise the haloid salts as being present to a considerable extent undecomposed in the flame, and acting as electrolytes, the fact that at high dilution the haloid salts and oxysalts alike of any one metal have the same conducting power, makes it probable that under these circumstances the haloid salts have also been converted into hydroxides, thus giving a common dissociating body.

The fact that potassium iodide at higher concentrations has a greater conductivity than potassium chloride, or bromide, is compatible with the greater readiness with which this salt is acted upon by oxidising agents. Whilst the chloride and bromide preserve their individuality, the iodide is largely converted into the oxide, which has a higher conductivity.

Coming lastly to the question whether the luminosity in flames coloured by salt vapours is connected with their electrical conductivity, we think our observations on flames containing chloroform give a definite decision in the negative.

The addition of chloroform to a flame produces hydrochloric acid. Now the conductivity of a flame containing either chloroform or hydrochloric acid, but no salt, is shown by our experiments (see p. 121) to be extremely small. Since in a flame containing an alkaline chloride the conductivity depends on the ionisation of this salt, the increased concentration of the chlorine ions due to the introduction of chloroform is so small that the degree of ionisation is not materially reduced and the conductivity therefore is not greatly affected.

The coloration of the flame is, however, entirely destroyed by the addition of chloroform.

We can say, therefore, that hydrochloric acid prevents the occurrence in the flame of the substance on which the emission of light depends, and that this substance is not merely the metal existing as an ion.

Thus the question which originally impelled us to our experiments is answered. Since it is answered in the negative, some other explanation of the luminosity of salt vapours must be sought, and we fall back upon the alternatives which have already been discussed by one of us on a previous occasion ('Phil. Mag.,' (V), 37, 245 (1894)).

It seems clear that the coloration of a flame containing vaporised sodium chloride is dependent upon the presence of the vapour of the metal in the non-ionic state, and the explanation of this, most conformable to our experiments, is that a very small proportion of the chloride is first converted into oxide by oxidising gases in the flame and the oxide then reduced by reducing gases in the flame. The presence of hydrochloric acid prevents the formation of oxide and hence prevents also the liberation of the metal. Whether the metal vapour glows solely in consequence of its high temperature, or because of vibrations imparted to its atoms during chemical change, is a question which our experiments were not designed to answer.

IV. *The Diffusion of Ions into Gases.*

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Communicated by Professor J. J. THOMSON, F.R.S.

Received April 25,—Read May 18, 1899.

INTRODUCTION.

THERE are several interesting results in connection with molecular physics which can be obtained from the coefficients of diffusion of ions into gases. From determinations of these coefficients we are enabled to find the number of molecules in a given volume of a gas, and to compare the charge on an ion in a conducting gas with the charge on a hydrogen ion in a liquid electrolyte. In the present paper the principles which are involved in the theory of the interdiffusion of gases are applied to the diffusion of ions produced in a gas by the action of Röntgen rays.

It will simplify matters if we first consider the general theory of the conductivity of gases. Professor THOMSON has shown that all the phenomena which are met with can be explained by supposing that the rays produce ions in the gas, the motion of which, when acted on by an electric force, gives rise to the observed conductivity. When the gas has been removed from the influence of the rays the conductivity gradually diminishes, and the disappearance of the ions may be due to three causes, any of which may predominate.

1. If an electric force is acting, the ions travel through the gas along the lines of force and are discharged when they reach the boundary.
2. Recombination destroys the conductivity; the positive and negative ions as they move about in the gas come into contact and thus neutralise one another.
3. The ions diffuse and come into contact with the sides of the vessel which contains the gas. This effect we shall denote as the effect of the sides. Like the recombination, it takes place when no electric forces are acting, and it is due to the motion of agitation of the ions.

In order to illustrate in a simple way the principles which are involved in the experiments which are described in the present paper, we will suppose that a gas is contained in a metal sphere and that it has been made a conductor by the action of

Röntgen rays. Let us consider what takes place when the gas has been removed from the action of the rays, disregarding for the present the effect of recombination. The ions may be considered as constituting a separate gas, the molecules of which may be either bigger or smaller than the molecules of the gas in which they are immersed. When an ion comes into contact with the surface of the sphere, it loses its charge, so that the metal may be regarded as a body which completely absorbs the ions. The reduction in the conductivity by the diffusion of the ions to the sides is exactly analogous to the removal of moisture from a gas by bubbling it through sulphuric acid. The more rapidly the water vapour diffuses through the gas, the greater will be the number of water molecules which come into contact with the acid round the bubble. If the quantity of moisture which is removed be found experimentally, the coefficient of diffusion of water vapour into the gas can be deduced.* It would be impracticable to use this method to find the coefficient of diffusion of ions into a gas contained in a large vessel, as the loss of conductivity due to recombination would be large compared with the loss due to the sides.

The method which was employed was to pass a uniform stream of gas through fine metal tubing, and to allow the rays to fall on the gas immediately before entering the tubing. The bore of the tubing can be so adjusted that the number of ions which come into contact with the sides will be large compared with the number which recombine.

It is convenient to use tubing of such a length that the conductivity will be reduced to about one-half its initial value.

In order to obtain the coefficient of diffusion, when the reduction in the conductivity is known, the following problem presents itself.

If a small quantity of a gas, A, is mixed with another gas, B, and the mixture passed along a tube, the sides of which completely absorb A, to find what quantity of A emerges from the tube with B.

It will be immediately seen that if the gases diffuse rapidly into each other, a large proportion of the molecules of the gas A will come into contact with the surface of the tube, and will there be absorbed. If on the other hand the rate of interdiffusion is very small, the molecules of A will travel down the tube in straight lines parallel to the axis of the tube, and practically none of them will come into contact with the surface.

The complete solution of the above problem, taking into account the variation of the velocity at points along a radius of the tube, is given in Section I. The results of the experiments and the conclusions to which they lead are contained in Section II.

* JOHN S. TOWNSEND, 'Phil. Mag.,' June, 1898.

SECTION I.

MATHEMATICAL INVESTIGATION.

1. In a conducting gas we have two distinct sets of bodies to deal with : the ions, which are charged, and whose motion under an electromotive force constitutes conduction, and the uncharged molecules, the number of which is very much greater than the number of ions [the latter number multiplied by 10^{12} gives about the order of the number of molecules]. The ions, which for the present we will suppose to consist of an equal number of positively and negatively charged carriers, may be considered as a distinct gas, A, and the rest of the molecules through which they move as another gas, B, the two together constituting a conducting gas. When the carriers come into contact with a metal surface, they either give up their charge to the metal or remain in contact with the surface, so that the metal behaves like a perfect absorber of the ions.

In a paper On the Dynamical Theory of Gases,* MAXWELL has given the general equations of motion of two gases diffusing into each other.

The equations are of the form :

$$\rho_1 \frac{du_1}{dt} + \frac{dp_1}{dx} = kA\rho_1\rho_2(u_2 - u_1) + X\rho_1,$$

where ρ_1 and ρ_2 are the densities of the gases; p_1 and p_2 their partial pressures; u_1 and u_2 their mean velocities in the x direction; kA a constant for the two gases which depends upon the temperature; and X the force acting on unit mass.

The first and last terms in the above equation may be omitted, as they are small compared with the other two, but in dealing with a gas which is made up of small charged bodies a new term must be introduced when electric forces are acting.

Thus the term $\rho_1 X$ arising from the force of gravity, for example, is $981 \times m_1 n_1$; where n_1 is the number of molecules of the first gas per cub. centim. and m_1 the mass of each (m_1 expressed in grammes is of the order 10^{-23}).

In order to estimate dp_1/dx roughly, we will suppose that the gases are contained in a tube of .15 centim. radius, and that $p_1 = 0$ at the surface. In this case $\frac{dp_1}{dx}$ will be of the order $\frac{p'_1}{.15}$, where p'_1 is the value of p_1 at the centre. Letting ξ_1 , η_1 and ζ_1 denote the mean velocities of agitation in the directions x , y , and z , $p'_1 = m_1 n'_1 \xi_1^2$, and we obtain $\frac{p'_1}{.15} = \frac{m_1 n'_1 \xi_1^2}{.15}$, which is large compared with $981 \times m_1 n'_1$, since ξ_1 is of the order 10^4 .

The first term $m_1 n_1 du_1/dt$ is small compared with dp_1/dx , since the resistance to the motion is so great; the acceleration in the cases with which we are concerned

* J. C. MAXWELL, 'Phil. Trans.,' vol. 157, 1866.

is less than the acceleration of a body falling under gravity, and consequently is of a much smaller order than dp_1/dx .

When each of the n_1 molecules of the first gas carries an atomic charge (6×10^{-10} electrostatic unit), forces come into play which may be of any order compared with $\frac{dp_1}{dx}$. In an electric field having a potential gradient of 1 volt per centim., the force on n'_1 ions would be $\frac{1}{300} \times 6 \times 10^{-10} \times n'_1$, which is large compared with the above value of $\frac{dp}{dx} \left[\frac{10^{-15} n'_1}{.15} \right]$.

In general six equations of the form given by MAXWELL are required, but when, as in the present case, one of the gases is present in very small quantities, the system of equations reduces to three, and the process of diffusion of the ions may be considered as having no effect on the mean velocities of the gas through which they diffuse. The second gas, B, has practically no motion in passing along a tube, except along the axis, which we take as coinciding with the axis of coordinates z . The notation can therefore be simplified, and in what follows we shall let n be the number of ions per cub. centim.; p , their partial pressure; e , the charge on each ion; X , Y , and Z , the electric forces at any point; u , v , and w , the velocities of the ions; W , the velocity of the gas, B, through the tube; (a) the radius of the tube; and K , the coefficient of diffusion of A into B.

The differential equations giving the motion are :—

$$\begin{aligned}\frac{1}{K} pu &= -\frac{dp}{dx} + nXe, \\ \frac{1}{K} pv &= -\frac{dp}{dy} + nYe, \\ \frac{1}{K} pw &= -\frac{dp}{dz} + nZe + \frac{1}{K} pW.\end{aligned}$$

When the steady state is reached, p is constant at any point in the tube with respect to the time, and the equation of continuity becomes

$$\frac{d}{dx}(pu) + \frac{d}{dy}(pv) + \frac{d}{dz}(pw) = 0.$$

dp/dz can be omitted from the third equation, as it is small compared with the other terms, thus, in practice, $\frac{1}{p} \frac{dp}{dz}$ is of the order $\frac{1}{20}$, $W = 100$, and $K = .03$; so that dp/dz is only about one ten-thousandth of $\frac{1}{K} pW$.

In the case with which we are dealing, $W = \frac{2V}{a^2} (a^2 - r^2)$, where V is the mean velocity defined by the condition, $\pi a^2 V t =$ total volume of the gas B, crossing any section in a time t . Confining the investigation to the case where the numbers of

positive and negative carriers are equal, the forces X, Y, and Z vanish, and the equation for p becomes:—

$$K \left(\frac{d^2 p}{dz^2} + \frac{d^2 p}{dy^2} \right) - \frac{2V}{a^2} (\alpha^2 - r^2) \frac{dp}{dz} = 0;$$

which, expressed in cylindrical coordinates, becomes

$$r^2 \frac{d^2 p}{dr^2} + r \frac{dp}{dr} - \frac{2Vr^2}{a^2 K} (\alpha^2 - r^2) \frac{dp}{dz} = 0 \quad \dots \quad (1).$$

We have to find a solution of this equation which will satisfy the conditions:

$p = p_0$ a constant when $z = 0$ for all values of r , since A is distributed evenly throughout B on entering the tube.

$p = 0$ when $r = a$ for all values of z , since A gets absorbed by coming into contact with the tube.

Let $p = \phi e^{-\frac{\theta^2 \alpha^2 K}{2V} z}$, where ϕ is a function of r , and θ^2 a constant to be determined afterwards.

Substituting this value of p in Equation (1), we obtain

$$r^2 \frac{d^2 \phi}{dr^2} + r \frac{d\phi}{dr} + \theta^2 r^2 (\alpha^2 - r^2) \phi = 0. \quad \dots \quad (2).$$

One solution, M, of this equation can be found in the form of a series.

Let

$$A_m r^m + A_{m+2} r^{m+2} + A_{m+4} r^{m+4}$$

be three consecutive terms in the expansion of M in powers of r .

Substituting in (2) we find, by equating to zero the coefficient of the $(m+4)^{\text{th}}$ power of r , that

$$(m+4)^2 A_{m+4} + \theta^2 \alpha^2 A_{m+2} - \theta^2 A_m = 0.$$

If $A_{m+4} r^{m+4}$ is the first term in M, $(m+4)^2$ must vanish. Hence, the first term must be a constant, which we will take as unity. Thus

$$M = 1 + B_1 r^2 + B_2 r^4 + B_3 r^6 + \&c. \quad \dots \quad (3),$$

where $B_1, B_2, B_3, \&c.$, are found from the equations

$$4B_1 + \theta^2 \alpha^2 = 0,$$

$$16B_2 + \theta^2 \alpha^2 B_1 - \theta^2 = 0,$$

$$36B_3 + \theta^2 \alpha^2 B_2 - \theta^2 B_1 = 0, \&c.$$

2. If Equation (3) be written in the form

$$M = 1 - \beta_1 \left(\frac{r}{a}\right)^2 + \beta_2 \left(\frac{r}{a}\right)^4 - \beta_3 \left(\frac{r}{a}\right)^6 + \&c. \dots,$$

the relation connecting any three consecutive coefficients becomes

$$4n^2\beta_n = \theta^2\alpha^4(\beta_{n-1} + \beta_{n-2}),$$

from which it is easy to see that the series we have found for M is convergent.

Let $2n$ be greater than $\theta^2\alpha^4$, and let $\beta_{n-1} + \beta_{n-2} = S$. Then

$$\beta_n < \frac{S}{2n}, \text{ and } \beta_{n+1} < \frac{S}{2n}.$$

Similarly,

$$\beta_{n+2} < \frac{S}{2n(n+2)}, \text{ and } \beta_{n+3} < \frac{S}{2n(n+2)}.$$

Proceeding in this way, we see that

$$\beta_{n+2m} < \frac{S}{2n(n+2)(n+4)\dots(n+2m)},$$

from which it follows that the series (3) is convergent.

3. The Equation (2) has a second independent solution, N , which can be found by using the solution $\phi = M$, the complete solution being $\alpha M + \beta N$. It will be seen from what follows that, when $r = 0$, N becomes infinite; so that it must be neglected when the gas A , as in the present case, extends to the centre of the tube.

Substituting for ϕ in Equation (2) $N = Mu$, we obtain

$$Mr^2 \frac{d^2u}{dr^2} + 2r^2 \frac{dM}{dr} \frac{du}{dr} + rM \frac{du}{dr} = 0,$$

or

$$\frac{1}{du/dr} \frac{d^2u}{dr^2} + \frac{2}{M} \frac{dM}{dr} + \frac{1}{r} = 0,$$

which, on integration, gives $rM^2 du/dr = c$. Hence

$$u = c \int \frac{dr}{rM^2}.$$

Expanding $\frac{1}{rM^2}$ in partial fractions, and integrating, we see that u has a term $c \log r$, so that N becomes infinite when $r = 0$.

Thus p cannot contain N in its expansion, and we get

$$p = \Sigma c_o M_o e^{-\frac{\theta^2 \alpha^2 K}{2V}} \dots \dots \dots (4).$$

The boundary condition, $p = 0$ when $r = a$, requires that such values of θ^2 be chosen as will make $M_0 = 0$ when $r = a$.

Substituting (a) for (r) in the function M , we obtain a function of $\theta^2 a^4$ with numerical coefficients. Let x_1, x_2, x_3 , &c., be the values of $\theta^2 a^4$ which satisfy the equation $M_{r=a} = 0$, and let $\theta_1, \theta_2, \theta_3$, &c., be the corresponding values of θ ; and equation (4) becomes

$$p = c_1 M_1 e^{-\frac{\theta_1^2 a^2 K}{2V}} + c_2 M_2 e^{-\frac{\theta_2^2 a^2 K}{2V}} + \text{&c.} \quad (5).$$

4. Before proceeding to determine the coefficients c_1, c_2 , &c., it is necessary to prove some general properties of the solution of the equation $\nabla^2 \phi + \theta_n^2 f(x, y, z) \phi = 0$; $f(x, y, z)$ being any function of x, y, z . Let ϕ_n and $\phi_{n'}$ be solutions corresponding to values θ_n and $\theta_{n'}$ of the parameter θ .

By GREEN'S theorem, we have

$$\iiint [\phi_n \nabla^2 \phi_{n'} - \phi_{n'} \nabla^2 \phi_n] dx dy dz = \iint \left(\phi_n \frac{d\phi_{n'}}{d\nu} - \phi_{n'} \frac{d\phi_n}{d\nu} \right) dS.$$

Let θ_n and $\theta_{n'}$ be such values of θ as will make ϕ_n and $\phi_{n'}$ vanish at the surface S of the region throughout which the above volume integral is taken. The surface integral vanishes under these conditions, and we get, on substituting for $\nabla^2 \phi_n$ and $\nabla^2 \phi_{n'}$ their values,

$$(\theta_n^2 - \theta_{n'}^2) \iiint \phi_n \phi_{n'} f(x, y, z) dx dy dz = 0 \quad (6a),$$

which shows that the triple integral vanishes when θ_n and $\theta_{n'}$ do not coincide.

Let us suppose $\phi_{n'}$ to be got from ϕ_n by changing θ_n^2 into $\theta_n^2 + d\theta^2$, and GREEN'S theorem gives

$$-d\theta^2 \iiint \phi_n^2 f(x, y, z) dx dy dz = d\theta^2 \iint \left[\phi_n \frac{d^2 \phi_n}{d\theta_n^2 d\nu} - \frac{d\phi_n}{d\theta_n^2} \frac{d\phi_n}{d\nu} \right] dS,$$

so that

$$\iiint \phi_n^2 f(x, y, z) dx dy dz = \iint \frac{d\phi_n}{d\theta^2} \cdot \frac{d\phi_n}{d\nu} dS \quad (6b).$$

We also have

$$\iiint \nabla^2 \phi_n dx dy dz = \iint \frac{d\phi_n}{d\nu} dS,$$

from which we derive

$$\theta_n^2 \iiint \phi_n f(x, y, z) dx dy dz = - \iint \frac{d\phi_n}{d\nu} dS \quad (6c).$$

5. Let $f(x, y, z)$ be $(a^2 - r^2)$ and ϕ a function of the cylindrical coordinate r . The equation $\nabla^2 \phi + \theta^2 f(x, y, z) \phi = 0$ then reduces to $\frac{1}{r} \frac{d}{dr} \left(r \frac{d\phi}{dr} \right) + \theta^2 (a^2 - r^2) \phi = 0$, so that we can substitute M for ϕ in the three equations (6a), (6b), and (6c). If the surface integrals be taken over the surface of the cylinder of radius a , we obtain

$$\int_0^a M_n M_{n'} (\alpha^2 - r^2) r dr = 0 \quad \dots \quad (7a).$$

$$\int_0^a M_n^2 (\alpha^2 - r^2) r dr = a \left[\frac{dM_n}{d\theta_n^2} \cdot \frac{dM_n}{dr} \right]_{r=a} \quad \dots \quad (7b).$$

$$\int_0^a M_n (\alpha^2 - r^2) r dr = -\frac{a}{\theta_n^2} \left[\frac{dM_n}{dr} \right]_{r=a} \quad \dots \quad (7c).$$

From these three equations the coefficients c_1 , c_2 , &c., can be determined.

Since $p = p_0$, when $z = 0$, we have

$$p_0 \equiv c_1 M_1 + c_2 M_2 + \&c.$$

Multiply this identity by $M_n (\alpha^2 - r^2) r dr$, and integrating from $r = 0$ to $r = a$, we obtain

$$-\frac{ap_0}{\theta_n^2} \left[\frac{dM}{dr} \right]_{r=a} = C_n \cdot a \left[\frac{dM}{dr} \frac{dM}{d\theta^2} \right]_{r=a}.$$

Hence

$$C_n = \frac{-p_0}{\theta_n^2 \left[\frac{dM_n}{d\theta_n^2} \right]_{r=a}},$$

and

$$p = -p_0 \left[\frac{M_1}{\theta_1^2 \left[\frac{dM_1}{d\theta_1^2} \right]_{r=a}} \cdot e^{-\frac{\theta_1^2 \alpha^2 K z}{2V}} + \frac{M_2}{\theta_2^2 \left[\frac{dM_2}{d\theta_2^2} \right]_{r=a}} \cdot e^{-\frac{\theta_2^2 \alpha^2 K z}{2V}} + \&c. \right] \quad \dots \quad (8).$$

On entering the tube the quantity of the gas A, per cub. centim., is proportional to p_0 , so that $p_0 \pi \alpha^2 V$ is proportional to the quantity of A entering the tube per second (which is found by the conductivity when A consists of ions). The quantity of A which crosses a section at a distance z from the origin per second is proportional to $\int_0^a p \times \frac{2V}{\alpha^2} (\alpha^2 - r^2) 2\pi r dr$, where p has the value given in Equation (8). The ratio R of the quantity of A which passes a section at a distance z to that which enters the tube is

$$\frac{4}{p_0 \alpha^4} \int_0^a p (\alpha^2 - r^2) r dr.$$

Substituting for p its value and using Equation 7 (c), we get

$$R = \frac{4}{\alpha^3} \left[\frac{1}{\theta_1^4} \left\{ \frac{dM_1}{dr} \right\}_{r=a} \cdot e^{-\frac{\theta_1^2 \alpha^2 K z}{2V}} + \frac{1}{\theta_2^4} \left\{ \frac{dM_2}{dr} \right\}_{r=a} \cdot e^{-\frac{\theta_2^2 \alpha^2 K z}{2V}} + \&c. \right] \quad \dots \quad (9).$$

The values of θ which are admissible are roots of the equation $M_{r=a} = 0$ regarded as an equation in θ .

[We may here point out that, if the gas, A, on entering the tube was distributed across the section according to the law $p = \chi(v)$, where χ denotes any function, the

coefficients, in the expansion of p in Equation (5), would be determinable by means of the identity

$$\chi(v) \equiv C_1' M_1 + C_2' M_2 + \&c.,$$

and by using 7 (a) and 7 (b) we see that

$$C_n' = \frac{\int_0^a \chi(r) M_n (a^2 - r^2) r dr}{a (dM_n/dr \cdot dM_n/d\theta^2)_{r=a}}.$$

Hence any function χ can be expanded in a series of the "M" functions.

It can further be seen from Equations 6 (a) and 6 (b) that $\chi(r)$ can be expanded in a series of functions ϕ , where ϕ is a solution of $\frac{1}{r} \frac{d}{dr} r \frac{d\phi}{dr} + \theta^2 f(r) \phi = 0$; those values of θ being selected which make ϕ vanish at the boundary of the cylinder to which χ applies.]

6. Before determining the roots of the equation $M_{r=a} = 0$, it will be found useful to establish the two following propositions:—

1. All the coefficients $\frac{1}{a^2 \theta_1^4} \left[\frac{dM/dr}{dM/d\theta^2} \right]_{r=a}$ in the expansion of R in Equation (9), are positive, and their sum is $\frac{1}{4}$.
2. All the roots of the Equation $M_{r=a} = 0$ are positive.

When $z = 0$, R must be unity, so that

$$\sum_{n=1}^{\infty} \frac{1}{a^2 \theta_n^4} \left[\frac{dM_n/dr}{dM_n/d\theta_n^2} \right]_{r=a} = \frac{1}{4}.$$

Also

$$\frac{1}{a^2 \theta_1^4} \left[\frac{dM_1/dr}{dM_1/d\theta^2} \right]_{r=a} = \frac{1}{a^2 \theta_1^4} \left[\frac{(dM_1/dr)^2}{dM_1/d\theta^2 \cdot dM_1/dr} \right]_{r=a} = \frac{1}{a^2 \theta_1^4} \int_0^a M_1^2 (a^2 - r^2) r dr \text{ by 7 (b).}$$

This last expression is essentially positive, since r is less than a , hence none of the coefficients in the series (9) can exceed ($\frac{1}{4}$ — sum of preceding coefficients).

The second proposition is easily proved by a geometrical method, which shows that when θ^2 is negative $M_{r=a}$ is a positive quantity greater than unity.

The first few terms in M are

$$M = 1 - \frac{\theta^2 a^2}{4} r^2 + \frac{1}{16} \left(\theta^2 + \frac{\theta^4 a^4}{4} \right) r^4 + \&c.$$

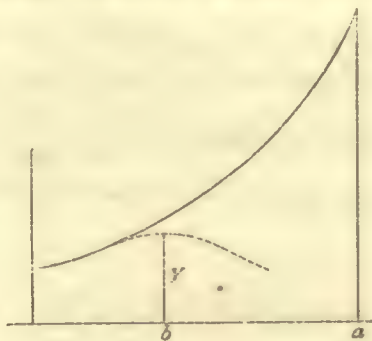
Let us suppose that θ^2 is negative, and let a curve be drawn, the x axis of which is r , and the y axis M .

When $x = 0 : y = 1$, $dy/dx = 0$, and d^2y/dx^2 is positive.

Hence the curve cuts the axis of y at unit distance from the origin, the tangent to the curve is here parallel to the axis of x , and as x increases the tangent begins to slope at a positive angle to the axis of x .

From the differential equation of the curve $x^2 \frac{d^2y}{dx^2} + x \frac{dy}{dx} = -\theta^2 (a^2 - x^2) x^2 y$, we can easily trace qualitatively the form that the curve takes as r is increased from 0 to a .

We have seen that initially, when x is small, y , dy/dx , and d^2y/dx^2 are positive quantities. Let us suppose that it is possible for dy/dx to be negative for any value of r less than a , the curve taking the form of the dotted line in the figure.



Before dy/dx , which starts with being positive, can become negative, it must pass through a zero value at $x = b$.

The differential equation then gives

$$b^2 \frac{d^2y}{dx^2} = -\theta^2 (a^2 - b^2) b^2 Y.$$

Hence d^2y/dx^2 is positive, therefore as we go along the axis of x in the positive direction from b , the tangent to the curve again begins to make a positive angle with the axis of x , so that y begins to increase. This shows that dy/dx cannot be negative at any point between $x = 0$ and $x = a$. Hence the curve must have a form somewhat similar to the continuous line in the figure, the value of y when $x = a$ being greater than the value of y at the origin. Hence the function $M_{r=a}$ cannot vanish for any negative value of θ^2 .

7. When r is made equal to a in M , the expression becomes a function of $\theta^2 a^4$, with numerical coefficients. The two smallest roots of the equation $M_{r=a} = 0$ are $\theta_1^2 a^4 = 7.313$, and $\theta_2^2 a^4 = 44.56$, which were found by expanding the function $M_{r=a}$ in ascending powers of $\theta^2 a^4$. For the determination of these roots, eight terms in the expansion were found; the larger roots cannot conveniently be found by this method, but for the purposes of this investigation their determination is not necessary, as the terms which they introduce into R are smaller than the experimental errors.

The other numbers which are required are

$$\begin{aligned} \frac{1}{\theta_1^2 a^3} \left[\frac{dM_1}{dr} \right]_{r=a} &= .1321, & \frac{1}{\theta_2^2 a^3} \left[\frac{dM_2}{dr} \right]_{r=a} &= .0302, \\ \frac{1}{a^4} \left[\frac{dM_1}{d\theta_1^2} \right]_{r=a} &= .0926, & \frac{1}{a^4} \left[\frac{dM_2}{d\theta_2^2} \right]_{r=a} &= .0279. \end{aligned}$$

Hence,

$$R = 4 \left[\frac{.1321}{7.313 \times .0926} e^{-\frac{7.313Kz}{2a^2V}} + \frac{.0302}{44.56 \times .0279} e^{-\frac{44.56Kz}{2a^2V}} + \&c. \right] \quad (10).$$

This formula holds for gases in general, when the gas which is being absorbed is present in small quantities. This restriction is necessary, since the effect of gravity would disturb the distribution of pressure given in equation (8), especially when the gases A and B differ much in density.

We therefore conclude that, when two gases, A and B, are mixed together and passed along a tube, the surface of which absorbs A, the ratio of the quantity of A which emerges to that which enters is

$$4 \left[.1952 e^{-\frac{7.313Kz}{2a^2V}} + .0243 e^{-\frac{44.56Kz}{2a^2V}} + \&c. \right],$$

where a is the radius of the tube, z its length, K the coefficient of interdiffusion of the gases A and B, and V the mean velocity of the gases in the tube.

The effect of the velocity being greater at the centre than at the surface of the tube, is to increase the quantity of A that comes through the tube with B. This can be seen* by comparing the formula (10) with the function

$$4 \left[\frac{e^{-\frac{(2.404)^2 Kz}{a^2V}}}{(2.404)^2} + \frac{e^{-\frac{(5.52)^2 Kz}{a^2V}}}{(5.52)^2} + \&c. \right],$$

which is the ratio of the quantity of A coming through the tube to the quantity entering, calculated on the supposition that the velocity of the gases is the same at every point.

If a gas, with ions uniformly distributed in it, has a conductivity c_1 after passing through a tube of length l_1 , and a conductivity c_2 after passing through a tube of length l_2 , we see from Equation (10) that

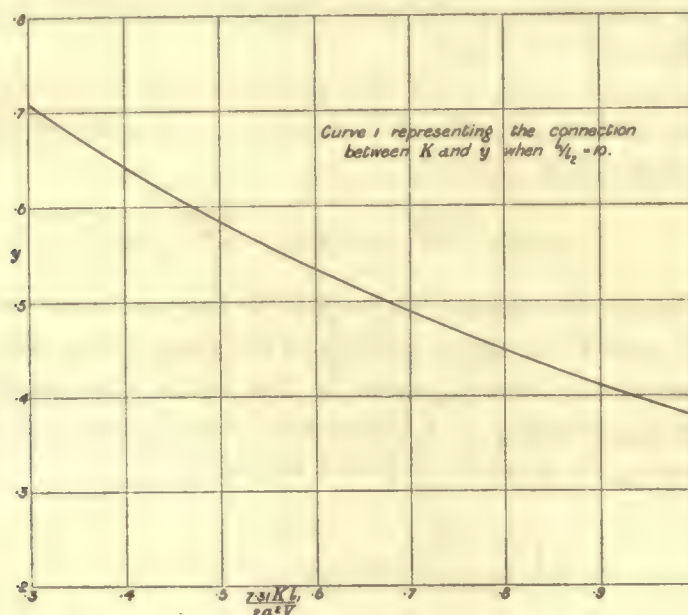
$$\frac{c_1}{c} = \frac{.195e^{-\frac{7.31Kl_1}{2a^2V}} + .024e^{-\frac{44.5Kl_1}{2a^2V}}}{.195e^{-\frac{7.31Kl_2}{2a^2V}} + .024e^{-\frac{44.5Kl_2}{2a^2V}}} \quad (11).$$

8. When the ionization is produced by Röntgen rays the ratio c_1/c_2 can be easily determined for most gases when $l_1 = 10$ centims., $l_2 = 1$ centim., $a = 1.5$ millim., and V about 100 centims. per second. Letting $c_1/c_2 = y$, and $\frac{7.31Kl_1}{2a^2V} = x$, the values of y corresponding to a series of values of x were found, and a curve representing the connection between x and y was drawn. The part of this curve which includes the values of y , which were obtained experimentally, is given in the first diagram, and from it the values of $\frac{7.31Kl_1}{2a^2V}$ can be immediately found.

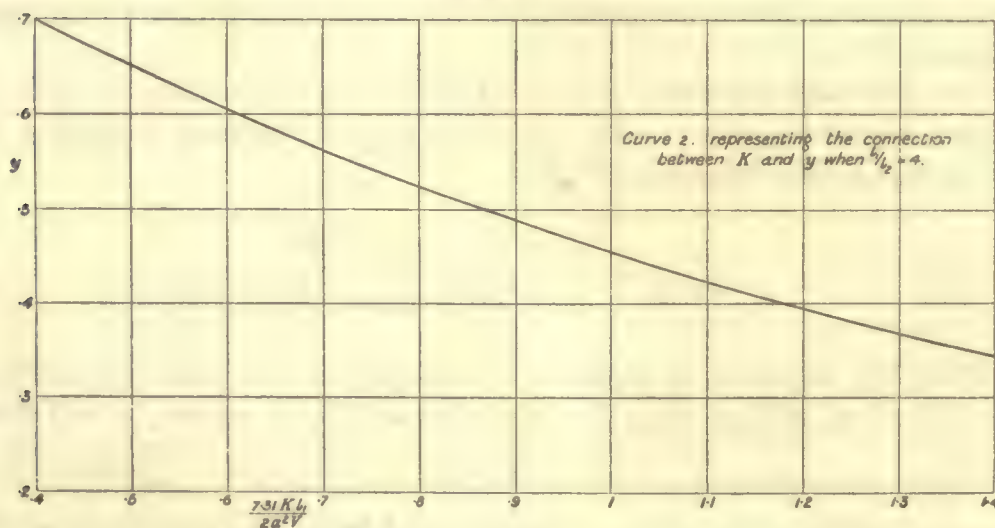
* JOHN S. TOWNSEND, 'Phil. Mag.,' June, 1898.

When hydrogen was passed through the tubing 10 centims. long it was found that its conductivity was so much reduced that it could not be accurately determined. It was therefore necessary to use another apparatus in which $l_1 = 4$ and $l_2 = 1$. The curve showing the connection between x and y for the case where $l_1/l_2 = 4$ is given in the second diagram.

Diagram 1.



Diagram' 2.



SECTION II.

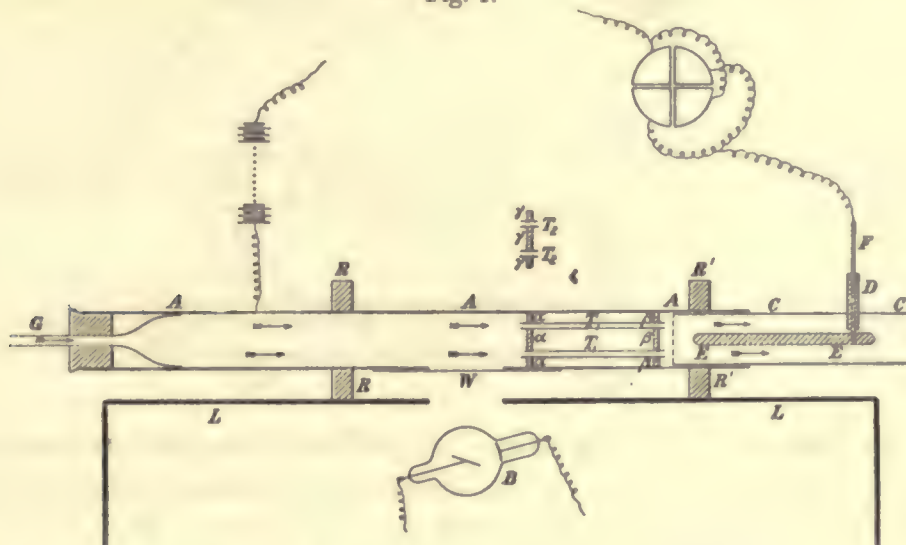
DESCRIPTION OF APPARATUS.

The apparatus which was used for experiments with air, is shown in fig. 1. It consisted of a brass tube, A, 50 centims. long and 3.2 centims. in diameter, with a

window, W, through which the rays from the Crookes tube, B, could pass. A second brass tube, C, 17 centims. long, fitted tightly into A, and could be moved into any desired position. The rod, F, to which the electrode, E, was fixed, passed through the ebonite plug, D, which insulated it from the tube C. The electrode, having no other support except D, could thus be put into any position in the tube A by moving C. A series of very fine wires ($\cdot 1$ millim. in diameter) were soldered parallel to one another, at distances 2 millims. apart, across the end of the tube C; the purpose served by this grating will be explained when we come to deal with recombination.

The gas entered the apparatus through the glass tube G, and, before reaching the electrode, passed through the tubes T_1 . These tubes were soldered into holes bored in two brass discs, α and β , which fitted exactly into the tube A, so that no gas could pass between the discs and the tube. The holes in the discs were equidistant from one another, and lay on a circle whose centre was the centre of the disc. Twelve tubes, 10 centims. long and $\cdot 3$ centim. in diameter, were thus arranged parallel to one another, two of which are shown in the figure. The symmetry of this arrangement ensured that the velocity along each of the small tubes would be the same. Another twelve tubes, 1 centim. long and $\cdot 3$ centim. in diameter, were soldered into the disc γ .

Fig. 1.



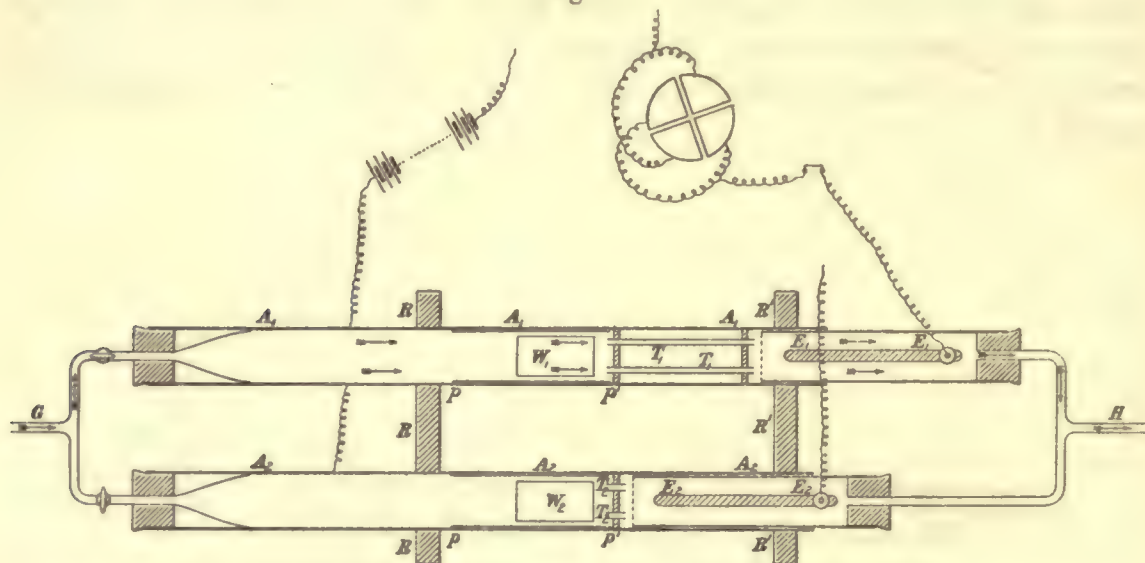
The bulb B, and the Ruhmkorff coil with which it was worked, were contained inside a box covered with lead, L. A rectangular hole was cut in the box and the lead, through which the rays from the bulb could pass. The lead covering prevented the rays from falling on any other part of the apparatus except the aluminium window W, and also screened the wire connecting F to the electrometer from electrostatic influence.

The tube A was supported by two ebonite rings, R and R', which rested on the lead, L, and insulated the tube. The potential of the tube was raised to 80 volts by

connecting it to a terminal of a battery of 40 lead cells, the other terminal of which was connected to earth. The electrode, E, was joined to a pair of quadrants of an electrometer, the other quadrants and the case being connected to earth.

In order to obtain a uniform stream of air, the tube, G, was connected to a gasometer, and the velocity of the gas along the tubes, T, could be calculated by observing the rate at which the cylinder of the gasometer fell. When the bulb is giving out rays, the gas, as it passes the aluminium window, becomes a conductor, and the ions are carried with the stream into the tubes T_1 . In passing through these tubes some of the ions are discharged by the sides, and the rest on coming into the field of force (caused by the difference of potential of 80 volts between the electrode and the tube C) are removed from the gas. It will be seen that no external force acts on the ions until they escape from the tubes T_1 , since all parts of the apparatus, except E, are in metallic connection with the large tube A.

Fig. 2.



When the potential of A is positive, the positively charged ions are collected on the electrode, and the deflection of the electrometer needle is proportional to the number of these ions, which come through the small tubes. The negative ions are collected on the electrode by making the potential of A negative.

If the motion of the gas past the electrode were steady, it would only require a difference of potential of a few volts between the electrode and the tube in order to remove all the ions from the gas. This, however, is not the case, since the motion of the gas as it escapes from the tubes, T, is turbulent, so that it is necessary to use a large force in order to get the maximum deflection on the electrometer scale. It was found that when the potential difference was changed from 80 to 40 volts, that the deflections were not appreciably altered; any voltage, therefore, between 40 and 80 would suffice to remove all the ions.

When it was required to find the conductivity of air after passing through short tubes, the tubes T_1 were removed and the disc γ was placed in the position occupied by α , then the electrode was moved up near the disc so that the electric force should act on the air immediately after leaving the tubes, T_2 .

Experiments with oxygen, hydrogen, and carbonic acid were made with the apparatus, the horizontal section of which is shown in fig. 2. It consisted of two long tubes, A_1 and A_2 , each exactly similar to A in fig. 1. In one of them the long tubes, T_1 , were set up, and in the other the tubes T_2 . The tubes, G and H , were connected to two gasometers, so that the gas could be passed from one to the other, through either of the tubes, A_1 or A_2 . The two tubes were fixed tightly into two rectangular pieces of ebonite, R and R' , which rested on the top of the box containing the bulb. Two wooden rails were screwed to the box at such a distance that the ebonite supports fitted exactly between them, so that, by sliding the apparatus from side to side, the window in either of the tubes could be brought exactly over the bulb.

It was found necessary to put a cylinder of aluminium inside each of the tubes, extending from p to p' , to prevent the rays from falling on the inner surfaces of the tubes, which were of brass. Before these cylinders were put in experiments were made to see whether the ionization produced in a stream of air passing along A_1 was equal to that produced in an equal stream through A_2 , and it was found that there was a considerable difference between the conductivities in the two cases. The inequality was not due to any difference in the thickness of the aluminium covering the two windows, but was traced to differences in the state of the surfaces of the brass tubes opposite the windows.

It has been shown by PERRIN* that the ionization produced by Röntgen rays in a gas in contact with a metal is considerably increased by allowing the rays to fall normally on the metal surface. This effect upon the ionization is different for different metals, and depends also upon the state of the surface. According to PERRIN, only a very small increase in conductivity is produced when the rays fall upon an aluminium surface. It was found that, when the two aluminium cylinders were put inside A_1 and A_2 , the difference in conductivity which was first observed disappeared entirely.

METHOD OF CONDUCTING THE EXPERIMENTS.

When working with the first form of apparatus the experiments were conducted in the following manner:—The tube A is raised to a potential of 80 volts positive, and the quadrants to which the electrode is joined are insulated. The stream of air from the gasometer is thus allowed to pass through the apparatus, and, when the velocity is steady, the coil working the bulb is turned on for a fixed time (20 seconds generally) and a deflection of n_1 divisions is obtained on the electrometer scale.

* 'Comptes Rendus,' vol. 124, p. 455.

The potential of A is then changed to 80 volts negative, and the same experiment is repeated and a negative deflection, n'_1 , is obtained.

The tubes, T_1 , are then removed, and the short tubes, T_2 , are put in their place as already described. Two similar experiments are then made, and larger deflections, n_2 and n'_2 , are obtained when the rays are turned on the same stream of air for the same time.

These four experiments are then repeated several times, and the mean value of the observations is taken in order to eliminate errors arising from variations in the strength of the rays. It was found that the constancy of the bulb was improved by allowing a fixed time (3 minutes) to elapse between each experiment. When this precaution was taken, it was possible to get rays which remained constant within 5 per cent. for the space of an hour.

When working with the second apparatus the numbers n_1 and n'_1 are obtained by sending the gas along the tube A_1 , and finding the deflections when the rays fall on the window, W_1 , for 20 seconds. In order to obtain n_2 and n'_2 it is only necessary to move the apparatus along the top of the box till the window in A_2 comes over the bulb, and to make similar observations with the electrode E_2 joined to the quadrants of the electrometer and the stream of gas passing along A_2 .

CORRECTION FOR RECOMBINATION.

Before the coefficients of diffusion can be calculated from the above observations it is necessary to make a correction for the loss of conductivity due to recombination. Let us denote by cn the number of ions which, when collected on the electrode, give a deflection of n divisions on the electrometer scale. The above experiments show that there are cn_2 positive ions which pass the section of the tubes, T_1 , at a distance of 1 centim. from the end near the window, W_1 . Of these cn_2 ions $c(n_2 - n_1)$ are lost in the remaining 9 centims. of the tubes. The loss is principally due to the ions coming into contact with the sides of the tubes; but the loss is also to a small extent due to collisions between positive and negative ions; it is necessary to find how much the observed value of n_1 must be increased in order to compensate for the loss of ions arising from recombination. If cM is the number of positive ions which encounter negative ions and do not come into contact with the sides, then the ratio $\frac{n_1 + M}{n_2} = y$ is the number which is required in order to calculate the coefficient of diffusion from the curve given in Section I. Recombination also takes place in the short tubes T_2 , but this effect is too small to take into account.

In order to find M it is necessary to find the rate at which the gas loses conductivity due to recombination, and this can be easily done by making a change in the arrangement of the apparatus. The tubes T_1 and T_2 were removed from A_1 and A_2 , and the electrodes were placed in the positions shown in fig. 2, the wire grating in front of the electrode E_1 being 12 centims. from the window in A_1 , and the grating in

front of E_2 3 centims. from the window in A_2 . The gratings in front of the electrodes, being in metallic connection with the tubes A_1 and A_2 , prevent the fields of force from extending up the tubes, so that when ions are produced in a stream of gas they are not acted upon by any force till they cross the grating.

A stream of gas is passed through the tube A_1 and the rays allowed to fall upon it for 20 seconds. The positive ions are collected on the electrode as before, and a deflection N_1 is obtained on the electrometer scale (it is not necessary in this case to make a similar experiment with the negative ions). The apparatus is then moved so as to bring the window W_2 over the bulb, and the stream of gas is sent through the tube A_2 , and the deflection N_2 , which is greater than N_1 , is obtained when the same experiment is made with the electrode E_2 joined to the electrometer. If d_1 and d_2 are the distances of the gratings from the windows W_1 and W_2 , we see that the conductivity falls from N_2 to N_1 , while the gas travels the distance $(d_1 - d_2)$. This reduction in conductivity is nearly entirely due to recombination, since the tubing is so wide that the loss due to diffusion to the sides is inappreciable. The mean time T that the gas takes to traverse the distance $d_1 - d_2$ can be found from the rate at which the gas escapes from the gasometer. It is important that this rate of escape should be the same as the rate of escape in the experiments in which n_1 and n_2 were determined, so that the ions should be distributed throughout the same volume of gas.

If cN is the number of ions in a gas in which no new ions are being produced, then the rate at which N varies with the time is given by the formula :

$$dN/dt = -aN^2,*$$

when no other influences except recombination contribute to the reduction in N .

Hence, by integration,

$$\frac{1}{N_1} - \frac{1}{N_2} = aT,$$

where T is the time in which the conductivity falls from N_2 to N_1 due to recombination. The value of a can therefore be determined by substituting the observed values of N_1 , N_2 , and T in this equation.

Returning to the case where the gas passes along the fine tubes, the conductivity falls from n_2 to n_1 while the gas passes along the last nine centims. of T_1 . Let θ be the average time that any portion of the gas takes to traverse these nine centims. The amount of ionization per cub. centim. of gas can easily be reduced so that the loss of conductivity due to recombination is only $\frac{1}{20}$ th of that due to diffusion to the sides.

From formula 10, Section I., we see that the conductivity n at any section of the tubes T_1 is given approximately by the formula :

* J. J. THOMSON and RUTHERFORD, 'Phil. Mag.,' November, 1896.

$$n = n_2 e^{-\beta t},$$

where t is the time occupied by the gas in travelling from the section where its conductivity is n_2 to the section where its conductivity is n .

From observation we have :

$$n_1 = n_2 e^{-\beta \theta},$$

so that

$$\beta = \frac{1}{\theta} \log \frac{n_2}{n_1}.$$

Let c_p be the number of positive ions which recombine with negative ions in the tubes T_1 . Then

$$dp/dt = \alpha n^2 = \alpha n_2^2 e^{-2\beta t},$$

and $p = 0$ when $t = 0$.

Let P be the value of p at the end of the tubes, the value of t being θ at that point.

By integration we obtain :

$$P = \alpha \frac{n_2^2 - n_1^2}{2\beta} = \alpha \theta \frac{n_2^2 - n_1^2}{2 \log \frac{n_2}{n_1}}.$$

Substituting for α its value this equation becomes

$$P = \frac{\theta}{T} \cdot \frac{n_2^2 - n_1^2}{2 \log \frac{n_2}{n_1}} \cdot \frac{N_2 - N_1}{N_1 N_2}.$$

The effect of recombination would obviously be over-corrected for if M were taken equal to P , for although cP ions are lost by encounters with others of opposite sign, still it must be remembered that, had no recombination taken place, some of these cP ions would have lost their charge to the sides of the tube. The number cM should only include those ions which encounter others of opposite sign, and would not subsequently come into contact with the sides if their rate of diffusion were unaltered by the collisions.

It is easy to see that M is less than P and greater than $\frac{n_1}{n_2} P$; a fairly accurate estimation of its value can be arrived at by the following method :—

At a section z of the tubes, where the conductivity is n , the number that recombine in a time dt is cdp , where $dp = \alpha n^2 dt$.

From the formula 10, Section I., it can be seen that of these cdp ions, $cdp \frac{n_1}{n}$ would not come into contact with the sides as they pass from z to the end of the tubes T_1 , if their rate of diffusion were unaltered by the recombination. Hence we have

$$\delta M = \delta p \frac{n_1}{n} = \alpha n n_1 \delta t = \alpha n_1 n_2 e^{-\beta t} \delta t.$$

We therefore obtain, by integration from $t = 0$ to $t = \theta$,

$$M = \frac{\alpha n_1 n_2 (1 - e^{-\beta \theta})}{\beta} = \frac{\alpha n_1 (n_2 - n_1)}{\beta}.$$

Substituting for α and β their values, this equation becomes

$$M = \frac{N_2 - N_1}{N_1 N_2} \times \frac{\theta}{T} \cdot \frac{n_1 (n_2 - n_1)}{\log \frac{n_2}{n_1}}.$$

CHARGE ACQUIRED BY THE GAS.

The deflections n_1 , which are obtained by collecting the positive ions after the gas has passed through the long tubes T_1 , are invariably greater than the corresponding negative deflections n_1' , which shows that the gas on issuing from the tubes T_1 has a positive charge proportional to $n_1 - n_1'$. In each of the tubes T_1 there is a small force arising from this charge, which repels the positive ions towards the sides and attracts the negative ions towards the axes of the tubes. It is only when the rays are strong that this force has any appreciable effect on the motion of the ions.

The deflections n_2 are also slightly greater than n_2' , but the difference between these numbers is not so great as the difference between n_1 and n_1' . The values which are obtained for the ratios $\frac{n_1 + M}{n_2}$ are greater than the corresponding values of $\frac{n_1' + M}{n_2'}$, which shows that the negative ions diffuse faster than the positive ions.*

It was found that the rates of diffusion of the positive and negative ions differed more when the gases were dry than when they were moist. Two sets of experiments were therefore made with each gas; in one set the gas was passed through large tubes of calcium chloride and entered the diffusion apparatus dry; in the other set the calcium chloride tubes were removed, and long tubes, partly filled with water, were put in their place. In all the experiments the gases passed through plugs of glass wool before entering the tubes A, in order to remove any dust that might be present.

RESULTS OF EXPERIMENTS WITH AIR.

The following tables give the numbers n_1 , n_1' , n_2 , and n_2' , which were obtained with different strengths of rays. The intensity of ionization was reduced to any required value by covering the hole in the lead with pieces of aluminium or zinc. Each experiment consists in determining the four electrometer deflections with a constant strength of rays. The positive and negative deflections n_1 and n_1' are given in the same column, the number in the upper line being n_1 and that in the lower n_1' . The corresponding observations n_2 and n_2' are arranged in a similar manner in the next

* J. ZELENY, 'Phil. Mag.,' July, 1898, describes an experiment to which he gives a similar interpretation.

column. M is the correction for recombination, which has to be added to n_1 and n_1' in order to obtain the ratios $\frac{n_1 + M}{n_2}$ and $\frac{n_1' + M}{n_2'}$, which are the required values of y .

The values of $\frac{7.31K \times 10}{2a^2V}$ are deduced from Curve I., Section I.; a^2V , the square of the radius of the tubing T multiplied by the velocity of the gas, is obtained by observing the rate of escape of the gas from the gasometer. The coefficients of diffusion of the ions into the gas are given in the last column.

Table I. gives the results of experiments with dry air, and Table II. the results obtained with moist air.

TABLE I. for Dry Air.

Experiment.		n_1 and n_1' .	n_2 and n_2' .	M.	y .	$\frac{73.1\text{ K.}}{2a^2\text{ V.}}$	$a^2\text{ V.}$	K.
I.	+	18.6	32.5	.5	.588	.495	2.06	.028
	-	13.0	29.1		.464	.76		.043
II.	+	63.6	118	4.0	.573	.525	2.06	.0296
	-	50.1	110		.491	.70		.0395
III.	+	128	262	22.0	.572	.525	2.06	.0296
	-	104	244		.516	.67		.038
Mean0346

We see that, as the strength of the rays is increased, the values of K for the positive ions appear to increase, and the values for the negative ions to diminish. It will be observed that the charge on the gas ($n_1 - n_1'$) varies from 5.6 to 24, and, as already explained, this charge acts in such a manner as to make the calculated value of K for the positive ions too big and that for the negative ions too small. The nearest value for the ratio of the coefficients of diffusion is therefore 1.54, as given by the first experiment.

Experiments were made to see whether consistent results would be obtained by varying the velocity V , and .036 was obtained for the mean value of K when a^2V was 1.57.

An experiment with air, made with the apparatus arranged for the other gases, gave the mean value of $K = .034$.

These values are as consistent as could be expected when all possible sources of error are taken into account.

TABLE II. for Moist Air.

Experiment.		n_1 and n_1' .	n_2 and n_2' .	M.	y .	$\frac{73.1 K}{2a^2 V}$.	$a^2 V$.	K.
I.	+	23.3	43	1.0	.563	.54	2.12	.031
	-	20.3	40		.532	.61		.035
II.	+	57.0	112.5	4.0	.542	.585	2.06	.033
	-	51.0	106		.515	.464		.036
III.	+	122.4	262	24.0	.559	.58	2.11	.032
	-	112	249		.546	.55		.035
Mean0335

These results show that the mean rate of diffusion is only slightly altered by the presence of moisture, but a large change is produced in the ratio of the coefficients of diffusion of positive and negative ions.

An experiment made with the apparatus shown in fig. 2 gave .034 for the mean value of K.

Oxygen.

The oxygen which was used was taken from a cylinder which contained about 94 per cent. of oxygen, the other 6 per cent. being principally nitrogen. The rates of diffusion of the ions through oxygen and air only differ by about 5 per cent., so that the presence of 10 per cent. of air would only increase the rate of diffusion by .5 per cent. No correction need therefore be made for the presence of nitrogen in the gas.

The experiments on diffusion gave results exactly similar to those obtained with air, except that the values of K were about 6 per cent. smaller.

The coefficients of diffusion which were obtained for positive and negative ions in dry oxygen are .025 and .0396 (mean .0323).

The corresponding numbers for the moist gas are .0288 and .0358 (mean .0323).

Carbonic Acid.

The carbonic acid which was used was taken from a cylinder. As in the case of oxygen, no correction need be made for the presence of a few per cent. of air mixed

with the gas. It would require 3 per cent. of air to make a difference of 1 per cent. in the coefficient of diffusion of the ions into carbonic acid.

The coefficients of diffusion which were obtained for the positive and negative ions in the dry gas are $\cdot 023$ and $\cdot 026$.

The corresponding numbers for the moist gas are $\cdot 0245$ and $\cdot 0255$.

The most remarkable difference between the diffusion in carbonic acid and other gases is that the rate of diffusion is nearly equal for the positive and negative ions. In oxygen, air, and hydrogen the rates of diffusion of the positive and negative ions differ by as much as 50 per cent. when the gases are dry, whereas in carbonic acid the difference amounts only to 12 per cent.

Hydrogen.

The hydrogen which was used was generated by the action of hydrochloric acid on zinc. The gas was bubbled through three strong solutions of caustic potash and potassium permanganate, in order to remove the acid vapour and the hydrocarbons, and collected in one of the gasometers. The purity of the gas was tested by finding its specific gravity, which is a very sensitive method of detecting the presence of other gases in hydrogen, since the density of the latter is so small. For this purpose a glass flask having a capacity of about 500 cub. centims. was used. Its volume was accurately found, and its loss of weight when dry hydrogen was substituted in it for dry air; from these two measurements the specific gravity of the gas could be calculated.

The presence of 1 per cent., by pressure, of air would alter the density by 14.5 per cent., which can be very easily detected, as 1 per cent. of air in a 500 cub. centim. flask weighs about 6 milligrammes. It was found that the specific gravity of the hydrogen which was prepared did not differ by 2 per cent. from the value $\cdot 00009$. After being in the gasometers and the diffusion apparatus for a few days the gas rose in density, due to air getting in. It would have been a matter of great difficulty to have made an apparatus, which had so many rubber joints, perfectly gas-tight, and it was considered simpler to find the amount of air in the hydrogen after each experiment, and to make a correction in the observed coefficient of diffusion.

We may here mention an experiment made with the same apparatus as was used for the determination of the rates of diffusion of the ions into oxygen and carbonic acid. The same velocity of gas in the tubing T was used, α^2V being 2.08. The positive and negative deflections obtained after the gas had passed through the tubes T_2 were 29 and 27.5, and the deflections after passing through the tubes T_1 were 6.5 and 2.2. This shows that in the last nine centimetres of the tubes T_1 the mean conductivity of the hydrogen fell from 28.2 to 4.3. An experiment with oxygen made with the same velocity, $\alpha^2V = 2.08$, showed that the mean conductivity of oxygen was reduced from 30.8 to 15.8. The difference in the behaviour of the ions

in the two gases cannot be attributed to a greater rate of recombination of ions in hydrogen, as other experiments show that the ions in hydrogen recombine somewhat slower than the ions in oxygen.

Another set of 12 tubes were therefore made, 4 centims. long, and of the same diameter as the tubes T_1 , and substituted in the apparatus shown in fig. 2 instead of the tubes T_1 . A series of experiments were made, and values of y were obtained which gave the ratios of the conductivities after the gas had passed through tubing 4 centims. and 1 centim. in length. The corresponding values of K were obtained from Curve II., Section I. In correcting for recombination in these experiments it is necessary to take into account the recombination in the tubes 1 centim. long.

The results obtained from experiments with dry hydrogen which contained 1·6 per cent. of air, are :

$$K = \cdot 117 \text{ for the positive ions,}$$

and

$$K = \cdot 181 \text{ for the negative ions.}$$

The coefficients of diffusion in a mixture containing 1·8 per cent. of air, 1·5 per cent. of water vapour, and 96·7 per cent. of hydrogen are : ·121 and ·134 for the positive and negative ions.

These results show that the rates of diffusion in hydrogen are 4·3 times as great as the rates of diffusion in air. In order, therefore, to obtain the coefficients of diffusion in pure hydrogen at atmospheric pressure, the above determinations must be increased by 3·3 per cent. for each per cent. of air in the gas.

Applying this correction, we obtain the following values for the coefficients of diffusion of the ions into hydrogen :

$$K = \cdot 123 \text{ for positive ions in dry hydrogen,}$$

and

$$K = \cdot 190 \text{ for negative ions in dry hydrogen.}$$

The corresponding coefficients for moist hydrogen are :

$$K = \cdot 128 \text{ for positive ions,}$$

and

$$K = \cdot 142 \text{ for negative ions.}$$

The coefficients of diffusion for the four gases which were examined are given in the following tables.

TABLE III.—Coefficients of diffusion of ions in dry gases.

Gas.	K for + ions.	K for - ions.	Mean value of K.	Ratio of the values of K.
Air	·028	·043	·0347	1·54
Oxygen	·025	·0396	·0323	1·58
Carbonic acid	·023	·026	·0245	1·13
Hydrogen	·123	·190	·156	1·54

TABLE IV.—Coefficients of diffusion of ions in moist gases.

Gas.	K for + ions.	K for - ions.	Mean value of K.	Ratio of the values of K.
Air	·032	·035	·0335	1·09
Oxygen	·0288	·0358	·0323	1·24
Carbonic acid	·0245	·0255	·025	1·04
Hydrogen	·128	·142	·135	1·11

REMARKS ON THE EXPERIMENTS.

The values of y which were found in these experiments are probably correct to 3 per cent., but on referring to the curves it will be seen that the error in K is larger than the error in y . For example, considering Curve I. at the point $y = \cdot 5$, it will be seen that a 4 per cent. error in y gives rise to a 6 per cent. error in K . We would therefore expect that the values of K are correct to about 5 per cent. In order to diminish y without changing the apparatus, the velocity of the gas in the tubing has to be diminished, and this has the effect of increasing in importance the correction for recombination. It was therefore considered best to use velocities of the blast which give y about $\cdot 5$.

It has been assumed that the velocity of the gas is given by the formula $W = \frac{2V}{a^2} (a^2 - r^2)$, and that the motion takes place in straight lines parallel to the axis of the tube. According to Professor REYNOLDS, the motion of a fluid in a tube is not in straight lines when the velocity exceeds a certain critical value, and eddies are produced even when the motion is initially in lines parallel to the axis. When the velocity is less than another critical velocity, any irregular motion will tend to return to the straight line motion. In order to ensure that the motion of any fluid, whose density is ρ , and viscosity μ , should tend to be in straight lines and obey the formula $W = \frac{2V}{a^2} (a^2 - r^2)$, the value of $V\rho a/\mu$ must be less than 700.

In the present experiments $V\rho a/\mu$ is less than 100, so that the velocities used are $\frac{1}{7}$ of the second critical velocity.

THE ATOMIC CHARGE.

The most interesting results which can be deduced from the coefficients of diffusion are obtained by comparing the velocity under an electromotive force with the coefficient of diffusion.

Considering one of the equations of motion

$$\frac{1}{K} pu = - \frac{dp}{dx} + nXe,$$

where e is the charge on the ion of the gas in electrostatic units, n the number of ions per cub. centim., and p their partial pressure, we see that when $dp/dx = 0$, the velocity u due to the electric force X is $\frac{nXeK}{p}$. If the potential gradient is 1 volt per centim., $X = \frac{1}{300}$ in electrostatic units, and the corresponding value of u is

$$u_1 = \frac{Ke}{300} \times \frac{n}{p}.$$

Let N be the number of molecules in a cub. centim. of a gas at pressure P , equal to the atmospheric pressure, and temperature 15° Centigrade, the temperature at which u_1 and K are determined.

The quotient N/P may be substituted for n/p in the above equation, and since the atmospheric pressure P in C.G.S. units is 10^6 , we obtain

$$Ne = \frac{3 \times 10^8 u_1}{K}.$$

If we take the values of u_1 from the table of mean velocities given by RUTHERFORD,* and the mean values of K obtained for dry gases, we get the following values of Ne :—

Air	$Ne_A = 1.35 \times 10^{10}$,
Oxygen	$Ne_o = 1.25 \times 10^{10}$,
Carbonic acid . . .	$Ne_c = 1.30 \times 10^{10}$,
Hydrogen	$Ne_H = 1.00 \times 10^{10}$,

Experiments on electrolysis show that 1 electrodynamic unit of electricity in passing through an electrolyte gives off 1.23 cub. centims. of hydrogen at temperature 15° Centigrade and pressure = 10^6 C.G.S. units. The number of atoms in this volume is $2.46 N$, so that if E is the charge on a hydrogen atom in the liquid electrolyte,

$$\begin{aligned} 2.46 NE &= 1 \text{ electromagnetic unit,} \\ &= 3 \times 10^{10} \text{ electrostatic units.} \end{aligned}$$

Hence

$$NE = 1.22 \times 10^{10},$$

the charge E being expressed in electrostatic units.

Since N is a constant, we conclude that the charges on the ions produced by Röntgen rays in air, oxygen, carbonic acid, and hydrogen are all the same, and equal to the charge on the hydrogen ion in a liquid electrolyte.

Professor THOMSON† has shown that the charge on the ions in hydrogen and oxygen, which have been made conductors by Röntgen rays, is 6×10^{-10} electrostatic unit, and is the same for both gases.

* E. RUTHERFORD, 'Phil. Mag.,' November, 1897.

† J. J. THOMSON, 'Phil. Mag.,' December, 1898.

Taking this value for the charge e , we obtain

$$N = 2 \times 10^{19}.$$

From this we deduce the weight of a molecule of hydrogen

$$4.5 \times 10^{-24} \text{ gramme.}$$

Every step in the theory by which these numbers are obtained is supported by direct experimental evidence.

Since, as we have just shown, the charge on an ion produced by Röntgen rays, is equal to the charge on a hydrogen ion in a liquid electrolyte, this latter charge is also 6×10^{-10} electrostatic unit.

Although the value of Ne for hydrogen is 25 per cent. different from its value for other gases, we are justified in including hydrogen in the above general conclusion, as we would expect the value of u_1 for hydrogen to be too small. RUTHERFORD makes no mention of having corrected for the presence of air in his apparatus, or of having used perfectly dry hydrogen. If we take the mean value of K for moist hydrogen, we obtain

$$Ne_H = 1.15 \times 10^{-10}.$$

In order to prove that the charge on the positive ion is equal to the charge on the negative ion, the ratio of the coefficients of diffusion must be shown to be equal to the ratio of the velocities. Professor ZELENY* has shown that the negative ions travel faster under an electromotive force than the positive ions, the ratio of the velocities being 1.24 for air and oxygen, 1.15 for hydrogen, and 1.0 for carbonic acid.

The experiments on diffusion show that the ratio of the velocities would be larger in dry than in moist gases, but as this point has not yet been examined by Professor ZELENY, we cannot expect a very close agreement between the ratios which he gives for the velocities and the ratios of the coefficients of diffusion.

We are led to conclude that the charges on the positive and negative ions are equal from another point of view. It has been proved that the mean charge is the same as the charge on an ion of hydrogen in a liquid electrolyte. If the charges differed, one of them would be less than the charge on the hydrogen ion, whereas experiments on electrolysis show that all ionic charges are either equal to the charge on the hydrogen ion, or an exact multiple of it.

COMPARISON OF THE RATES OF DIFFUSION OF THE IONS WITH THE RATES OF INTERDIFFUSION OF GASES AND VAPOURS.

The coefficients of diffusion of ions into a gas are much smaller than the coefficients

* J. ZELENY, 'Phil. Mag.,' July, 1898.

of diffusion of gases into each other, but do not differ much from the coefficients of diffusion of vapours into gases.

We give here a table of the latter coefficients, so that they may be compared with the numbers given in Tables III. and IV.

TABLE V., giving Coefficients of Diffusion of some Gases and Vapours into Air, Carbonic Acid, and Hydrogen.

Gas or vapour.	Air.	Carbonic acid.	Hydrogen.	Observer.
Oxygen	·18	·721	LOSCHMIDT
Carbonic acid	·142	...	·555	
Æther	·077	·055	·29	WINKELMANN
Alcohol	·101	·068	·378	
Water	·198	·132	·687	

The experimental results show that if K is the coefficient of interdiffusion of two gases whose densities are ρ_1 and ρ_2 , $K \times \sqrt{\rho_1 \rho_2}$ is roughly constant. The rates of diffusion of the ions are roughly inversely proportional to the square roots of the densities of the gases.

Two theories have been suggested to account for the small values which have been found for the rates of diffusion of the ions into a gas.

The effect may be explained if we suppose that a number of molecules surround the ion. The carriers of the charge would then diffuse slowly like a gas made up of large molecules. The mass of the group could be found by comparing the rates of diffusion of the ions with the rates of interdiffusion of gases. A rough calculation shows that the mass of this group should be about 30 times the mass of a molecule of oxygen.

The small values of the coefficients of diffusion may also be explained if we suppose that the carrier is as small as a molecule of the gas, and that the electric force exerted on the molecules which approach it gives rise to encounters which would not have taken place if the carrier were uncharged.

If we adopt the theory that the ions are surrounded by molecules forming a sphere which moves about with the ion, we can apply MAXWELL'S formula for the coefficient of interdiffusion of two gases to find the radius of the sphere.

The coefficient of interdiffusion of two gases, according to the theory founded on the collisions of elastic spheres, is

$$D_{12} = \frac{1}{2\sqrt{6\pi}} \cdot \frac{V}{N} \cdot \sqrt{\frac{1}{w_1} + \frac{1}{w_2}} \cdot \frac{1}{S_{12}}^*$$

where w_1 and w_2 are the molecular weights of the two gases, that of hydrogen being unity.

* J. C. MAXWELL, 'Nature,' vol. 8.

S_{12} is the distance between the centres of the molecules at collision in centimetres.

V is the "velocity of mean square" of a molecule of hydrogen at 0° C.

$$V = \sqrt{(3p/\rho)} = 186000 \text{ centims. per second.}$$

N is the number of molecules in a cubic centimetre at 0° and 760 millims. pressure.

Taking the value of N , which we have found, 2×10^{19} , we see that

$$D_{12} = 1.1 \times 10^{-15} \sqrt{\left(\frac{1}{w_1} + \frac{1}{w_2}\right) \frac{1}{S_{12}^2}}.$$

If the carrier of the charge is large compared with the molecule, S_{12} will be the radius of the carrier and $1/w_2$ will be small compared with $1/w_1$.

Letting $D_{12} = .156$, the coefficient of diffusion of ions into hydrogen, $w_1 = 1$, we obtain for the radius of the ion in hydrogen

$$S = \sqrt{\frac{1.1 \cdot 10^{-15}}{.156}} = 8.2 \times 10^{-8}.$$

A similar calculation shows that the radius of an ion in oxygen is

$$9.2 \times 10^{-8}.$$

Adopting the second theory which we have proposed to account for the slowness of the rates of diffusion of the ions, and applying the same formulæ, the values of S will be greater than the above values by the factor $\sqrt{2}$, since the terms $1/w_1$ and $1/w_2$ are of the same order.

The values obtained in this way for S_{12} would denote the distance that a molecule of the gas must approach an ion in order that the electric force should appreciably alter its motion.

RECOMBINATION.

The results of the experiments which were made to determine the rate of recombination are given in the following table. T is the time, in seconds, in which the conductivity falls from N_2 to N_1 , and V is the volume, in cub. centims., of gas which was used in each experiment.

TABLE VI.

Gas.	N_2 .	N_1 .	T .	V .	Correction to be added to N_1 .
Air	77	43	.93	1540	3
Oxygen	59.5	37	.95	1520	2
Carbonic acid . . .	62.5	39	.90	1590	2
Hydrogen	117	85	.275	1360	5

The numbers N_1 and N_2 are the electrometer deflections obtained in the manner described above. In the first three gases the electrode E_1 was at a distance 12 centims. from the window W_1 , and the electrode E_2 at a distance 3 centims. from the window W_2 . The conductivity therefore fell from N_2 to N_1 while the gas passed through 9 centims. of the tube A_1 .

The position of the electrodes had to be altered for hydrogen, as this gas would have lost about 16 per cent. of its conductivity, due to diffusion to the sides alone, in passing along 9 centims. of the wide tubing. The electrodes were therefore put at distances 3 and 6 centims. from the windows, and the strength of the ionization was increased.

The correction given in the tables is to compensate for the loss of conductivity arising from diffusion.

The electrometer was standardised, and it was found that each division corresponded to a charge of .0042 electrostatic unit. If e is the charge on the ion, the number of ions in a cub. centim. is $\frac{N \times .0042}{eV}$, which we will denote by v .

From the theory of recombination we have

$$dv/dt = \beta v^2, \quad \text{or} \quad \frac{1}{v_2} - \frac{1}{v_1} = \beta T.$$

From the numbers given in Table VI. we can obtain the values of β for the different gases. We thus find that for air, oxygen, carbonic acid, and hydrogen the values of β are, $3420 \times e$, $3380 \times e$, $3500 \times e$, and $3020 \times e$.

The rates of recombination in air, oxygen, and carbonic acid are practically the same, and about 15 per cent. greater than the recombination in hydrogen.

Substituting for e its value, we obtain for the first three gases $\beta = 2 \times 10^{-6}$, *q.p.*

We can now find how near two ions of opposite sign must approach each other in order to recombine. If there are v positive ions, and v' negative ions, in a cub. centim., the number that recombine in a time δt is $vv'\beta\delta t$.

The number of negative ions that approach within a distance S of positive ions in the same time can be found from the kinetic theory of gases.

MAXWELL has shown* how to calculate the number of times per second a molecule of one gas will come within a distance R of the molecules of another gas.

This number is

$$2n \sqrt{\pi} \sqrt{(\alpha^2 + \beta^2)} R^2,$$

where n is the number of molecules per cub. centim. of the second gas, $\alpha^2 = \frac{2}{3} v_1^2$, $\beta^2 = \frac{2}{3} v_2^2$, v_1^2 and v_2^2 are the mean squares of the velocities of agitation of the two gases.

We will suppose that an ion has the same mass as a molecule of the gas in which

* 'Phil. Mag.,' January and July, 1860.

it is produced. The mean square of the velocity of agitation of the ions will, on this hypothesis, be equal to the mean square of the velocity of agitation of the molecules of the gas. v_1^2 and v_2^2 will then be equal to 4.7×10^4 for the ions in oxygen.

The number of negative ions that approach within a distance R of positive ions in the time δt will be

$$2vv' \sqrt{\pi} \sqrt{\frac{2}{3}} (v_1^2 + v_2^2) R^2 \delta t.$$

Equating this number to the number that recombine in the same time we obtain

$$R = \frac{1}{3} 10^{-5} \text{ centim.}$$

At a distance $\frac{1}{3} 10^{-5}$ the charge on an ion would exert a force equal to a fall of potential of 16,200 volts. per centim. This force would make two oppositely-charged ions move towards each other with a velocity of 2×10^4 centims. a second.

It would be premature to discuss any further the results which have been obtained, as experiments are being carried out which may throw additional light upon the subject.

In conclusion, I wish to state that I am greatly indebted to Professor THOMSON for his advice and suggestions during the course of these investigations.

V. *On the Vibrations in the Field round a Theoretical Hertzian Oscillator.*By KARL PEARSON, *F.R.S.*, and ALICE LEE, *B.A., B.Sc.*, *University College, London.*

Received January 2,—Read January 19,—Revised May 14, 1899.

[PLATES 1-7.]

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(1.) Although HERTZ realised very fully* that his oscillator did not give “perfectly regular and long continued sine-oscillations,” and although BJERKNES† determined so long ago as 1891 the general form of the damping, it does not appear that HERTZ’s original investigation of the nature of the vibrations in the field round one of his oscillators has hitherto been modified. Indeed, his diagrams of the wave motion have been copied into more than one text-book,‡ and have usually been taken to represent what actually goes on in the surrounding field. Actually not only the diagrams, but

* “On very rapid Electric Oscillations,” ‘Wied. Annal.,’ vol. 31, p. 421, ‘Electric Waves,’ p. 49.

† ‘Wied. Annal.,’ vol. 44, pp. 74, 513-526. The damping of the oscillation in four or five periods is very marked.

‡ For example, ANDREW GRAY, ‘Absolute Measurements in Electricity and Magnetism,’ vol. 2, p. 734.

Hence,

$$f_2 = A_1 e^r + A_2 e^{-r},$$

where A_1 and A_2 are constants and

$$\psi = \frac{A_1 e^{p(t+ar)} + A_2 e^{-p(t-ar)}}{apr}.$$

Take only an *outgoing* wave and write $p = -p_1 + p_2 \sqrt{-1}$, hence

$$\psi = \frac{B}{r} e^{-p_1(t-ar)} \sin p_2(t-ar) \quad \dots \dots \dots (iv)$$

where t must be $> ar$, or $\psi = 0$.

$1/a$ is clearly the wave velocity v . Take $p_2 = \frac{2\pi}{\lambda} v$, then

$$\psi = \frac{B}{r} e^{-p_1(t-ar)} \sin \frac{2\pi}{\lambda} (vt - r) \quad \dots \dots \dots (v).$$

For typical oscillators $2\pi p_1/p_2$ seems to vary from $\cdot 3$ to $\cdot 5$, hence $p_1 = \cdot 3$ to $\cdot 5 \times v/\lambda$, or we see that if r be small as compared with λ , then

$$\psi = \frac{B}{r} e^{-p_1 t} \sin p_2 t.$$

Now, if X, Y, Z be the three components of electric force, we easily find

$$X = -\frac{d}{dx} \left(\frac{d\psi}{dz} \right), \quad Y = -\frac{d}{dy} \left(\frac{d\psi}{dz} \right), \quad Z = -\frac{d}{dz} \left(\frac{d\psi}{dz} \right),$$

or they are the three components of a "potential function"

$$V = B e^{-p_1 t} \sin p_2 t \frac{d}{dz} \left(\frac{1}{r} \right).$$

Take $B = -El$, and we see that V is the potential* due to a "double point" of moment oscillating between $+El e^{-p_1 t}$ and $-El e^{-p_1 t}$; thus the maximum charges rapidly diminish with the time. In fact, we have a system entirely analogous with that of HERTZ, except for this rapid diminution of the maximum charges with the time. It is in this running down of the maximum charges that the damping effect of the oscillator consists.

(3.) We shall now proceed to find the forces.

In the first place let us find the value of $\rho d\psi/d\rho$, which, following HERTZ, we will term Q . Then the components of electric and magnetic force can all be found by simple differentiation of Q , i.e.,

$$Z = \frac{1}{\rho} \frac{dQ}{d\rho}, \quad R = -\frac{1}{\rho} \frac{dQ}{dz}, \quad \text{and} \quad P = \frac{a}{\rho} \frac{dQ}{dt} \quad \dots \dots \dots (vi).$$

* To use HERTZ's language, see 'Electric Waves,' p. 142, and compare MAXWELL, vol. 1, § 129.

We have

$$\begin{aligned} Q &= \rho \frac{d\psi}{d\rho} = \rho \frac{d\psi}{dr} \frac{dr}{d\rho} = \frac{\rho^2}{r} \frac{d\psi}{dr} \\ &= -\frac{p^2 E l}{r} \frac{d}{dr} \left\{ \frac{e^{-p_1(t-ar)}}{r} \sin p_2(t-ar) \right\} \\ &= -\frac{\rho^2}{r^2} E l e^{-p_1(t-ar)} \left\{ \left(p_1 a - \frac{1}{r} \right) \sin p_2(t-ar) - a p_2 \cos p_2(t-ar) \right\}. \end{aligned}$$

Now put $p_1 = \eta \sin \chi$, $p_2 = \eta \cos \chi$; then if $\rho = r \sin \theta$, we have

$$Q = E l a p_2 \sin^2 \theta e^{-p_1(t-ar)} \left\{ \frac{\cos [p_2(t-ar) + \chi]}{\cos \chi} + \frac{\sin p_2(t-ar)}{r a p_2} \right\} \quad \text{. . . (vii).}$$

In our notation HERTZ finds*

$$Q = E l a p_2 \sin^2 \theta \left\{ \cos p_2(t-ar) + \sin \frac{p_2(t-ar)}{r a p_2} \right\} \quad \text{. . . . (viii).}$$

It is clear that the damped wave train, such as actually occurs with the Hertzian oscillator, makes very considerable changes in the form of Q . Thus:

(a.) As we might expect the damping factor $e^{-p_1 t}$ is introduced, or rather a damping factor $e^{-p_1(t-t_0)}$ where t_0 is the time at which the disturbance reaches a distance r from the centre of the oscillator. Clearly the factor $e^{p_1 a r}$ will sensibly modify the form of the lines of electric force obtained by tracing the curves

$$Q = \text{constant.}$$

(b.) The first term in the curled brackets is also sensibly modified both as to amplitude and phase.

The reader must not imagine that the difference between the formulæ (vii) and (viii) marks as soon as the vibrations are set up a great difference in the lines of electric force. All we contend for is that it marks a sensible difference in the shape after a few periods, and that this difference increases with the length of time and the distance of the part of the field considered from the oscillator. In fact loops which would remain at the end of each period finite according to formula (viii), have to shrivel up into points and disappear from the field altogether.

Suppose $2\pi p_1/p_2 = \cdot 4$, then $\tan \chi = \cdot 2/\pi$, and we find $\chi = 3^\circ 38' 33'' \cdot 3$, while $\sec \chi = 1\cdot 002,0244$. Hence, the amplitude of the cosine term is increased by about 2 per thousand, and the phase by 3° to 4° . It is the factor $e^{p_1 a r}$, however, which produces most sensible change. For $p_1 a = \frac{p_1 (\text{period})}{(\text{wave length})} = \cdot 4/\lambda$, if λ be the wave length. Now, if λ be 9·60 metres,† which was about its value for one of HERTZ's oscillators

* It seems better to write $p_2(t-ar)$ than $p_2(ar-t)$ with HERTZ, because ar must be less than t , or $Q = 0$, 'Electric Waves,' p. 142.

† HERTZ's λ is $\frac{1}{2}$ (wave-length). Considerable confusion has arisen from this in various translations of his papers. He assumes $\lambda = 4\cdot 8$ metres, i.e., a wave-length = 9·6.

(‘Electric Waves,’ p. 150), we should have at 12 metres distance from the oscillator $e^{ip_1 r} = \sqrt{e} = 1.649$, a factor which can very considerably modify Q as a function of r , if t be not equal to ωr , i.e., if the disturbance have not just reached that point of the field.

Expressing Q in terms of the wave-length λ , and the period 2τ , we have

$$\frac{Q}{2\pi E l / \lambda} = \sin^2 \theta e^{-\nu(t/2\tau - r/\lambda)} \left\{ \frac{\cos \left[2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \chi \right]}{\cos \chi} + \frac{\sin 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right)}{2\pi r / \lambda} \right\} \quad (\text{ix}),$$

where $\nu = 2\pi p_1 / p_2 = p_1 \times 2\tau$.

Thus we may write

$$\frac{Q}{2\pi E l / \lambda} = \phi \left(\theta, \frac{r}{\lambda}, \frac{t}{\tau} \right),$$

where ϕ is a known function.

The next stage was to plot for a reasonable value of ν , the curves $\phi = \text{constant}$ for a series of values of Q at different intervals of time. In order to show the decadence of the strength of the field in the neighbourhood of the oscillator, t was given the 56 successive values $\frac{1}{4}\tau, \frac{2}{4}\tau, \frac{3}{4}\tau, \tau, \frac{5}{4}\tau, \dots, 13\frac{3}{4}\tau, 14\tau$; or the field-changes were traced for seven complete oscillations, at intervals of $\frac{1}{8}$ oscillation. This was done for a sphere of $1\frac{1}{4}$ wave-lengths round the oscillator, or taking the wave-length to be 9.6 metres, for a sphere of 12 metres radius round the centre of the oscillator.*

Values of $Q\lambda/(2\pi E l)$ were chosen so as to give eight systems of curves with relative intensities

$$50, \quad 30, \quad 10, \quad 1, \quad -1, \quad -10, \quad -30, \quad -50.$$

In the accompanying diagrams (Plates 1-7) the fine continuous curves† give the ± 50 intensity, the fine dotted curves the ± 30 , the heavy continuous curves ± 10 , and the heavy dotted curves ± 1 . The outermost circle in each case is the boundary of the field explored; the innermost circle corresponds to the boundary of the area round the oscillator, within which it would hardly be legitimate to consider the oscillator a double electric point. The remaining circles are those for which $Q = 0$, and which separate positive from negative portions of the field. In the spaces between these circles the field must be considered to have alternative positive and negative intensity. It must of course be borne in mind that the curves only give a meridian section of the surfaces of equal intensity.

The work of calculating, plotting, and drawing such a long series of curves was

* HERTZ's diagrams only extend for three-quarters of a wave-length round the oscillator. Our diagrams suffice in extent to show the detachment of the loops preparatory to their outward propagation.

† The actual selection of fine and heavy, continuous and dotted curves to represent the several intensities, is due to the engraver working on the photographs of the original coloured diagrams. For special aid in the preparation of the diagrams and in their reproduction by photography, we have to heartily thank Messrs. E. WRENN and A. WHEELER respectively.

laborious, but as no investigation had been made of the damping out of an electromagnetic field, the work seemed worth undertaking. Some remarks may be made on the methods by which the arithmetic was carried out.

The equation to the curve being written

$$\sin^2 \theta = c \times \psi(r),$$

where $c = Q\lambda/(2\pi El)$ and

$$\psi(r) = e^{\nu(t/2\tau - r/\lambda)} \left\{ \frac{\cos \left[2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) \chi \right]}{\cos \chi} + \frac{\sin 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right)}{2\pi r/\lambda} \right\}^{-1},$$

c was given the values $\frac{1}{100}$, $\frac{1}{10}$, $\frac{3}{10}$, $\frac{1}{2}$, and the limiting values of r ascertained, for which θ was real. r was then given a series of values between these limits altering by small differences, and the values of $\sin \theta$ calculated; frequent values of r were taken at portions of the curve where it was found to be turning, and thus a close approximation found to its form. The original diagrams on a scale of a metre to the inch were formed by joining up the calculated points and painting in the curves so formed. These were afterwards reduced by photography.*

The dying out of a part of the field of a particular strength is well illustrated in the diagrams. Take the dying out of strengths greater than ± 50 represented by the fine continuous line. In fig. 25 we see the last sensible loop of the field containing greater strengths than this passing away. Up to fig. 33 we can still trace this portion of the field as a dot. But in fig. 29 the oscillator has ceased to give fresh centres even of this strength, and in fig. 34 they have passed away entirely. Figs. 30 to 41 give the shrinking up and final disappearance of parts of the field with a strength greater than ± 30 . Figs. 53 to 56 show the outward passage of the last loop of the field with a strength greater than ± 10 , and another ten diagrams would have sufficed to show no trace of strengths greater than ± 1 .

(4.) We will now proceed to find the electric and magnetic forces from (vi).

First, the electric force, Z , in direction of the axis of the oscillator :

$$Z = \frac{El \left(\frac{2\pi}{\lambda} \right)^3 e^{-\nu(t/2\tau - r/\lambda)}}{2\pi r/\lambda} \left[\sin^2 \theta \frac{\sin \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + 2\chi \right\}}{\cos^2 \chi} + (2 \cos^2 \theta - \sin^2 \theta) \right. \\ \left. \times \frac{\cos \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \chi \right\}}{(2\pi r/\lambda) \cos \chi} + (2 \cos^2 \theta - \sin^2 \theta) \frac{\sin \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) \right\}}{(2\pi r/\lambda)^2} \right] \quad (x).$$

Second, the electric force, R , perpendicular to the axis of the oscillator :

* The diagrams have lost very considerably in the process of photography and engraving. It may possibly be that some of the finer loops and dots will appear not at all, or at least unclearly, after the blocks have been somewhat used. We hope shortly to have kinematograph films of the original diagrams available.

$$R = \frac{El \left(\frac{2\pi}{\lambda} \right)^3 e^{-\nu(t/2\tau - r/\lambda)}}{2\pi r/\lambda} \sin \theta \cos \theta \left[- \frac{\sin \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + 2\chi \right\}}{\cos^2 \chi} \right. \\ \left. + \frac{3 \cos \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \chi \right\}}{(2\pi r/\lambda) \cos \chi} + \frac{3 \sin 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right)}{(2\pi r/\lambda)^2} \right] \quad (\text{xi}).$$

Now let

$$\phi_1(r, t) = \frac{El \left(\frac{2\pi}{\lambda} \right)^3 e^{-\nu(t/2\tau - r/\lambda)}}{2\pi r/\lambda} \left[\frac{\sin \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + 2\chi \right\}}{\cos^2 \chi} - \frac{3 \cos \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \chi \right\}}{(2\pi r/\lambda) \cos \chi} \right. \\ \left. - \frac{3 \sin 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right)}{(2\pi r/\lambda)^2} \right] \dots \dots \dots (\text{xii}),$$

and

$$\phi_2(r, t) = \frac{El \left(\frac{2\pi}{\lambda} \right)^3 e^{-\nu(t/2\tau - r/\lambda)}}{2\pi r/\lambda} \left[\frac{2 \cos \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \chi \right\}}{(2\pi r/\lambda) \cos \chi} + \frac{2 \sin 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right)}{(2\pi r/\lambda)^2} \right] \quad (\text{xiii}).$$

Then ϕ_1 and ϕ_2 are constant over any spherical surface about the centre of the oscillator at any time, and

$$\left. \begin{aligned} Z &= \phi_1 \sin^2 \theta + \phi_2, \\ R &= -\phi_1 \sin \theta \cos \theta, \end{aligned} \right\} \dots \dots \dots (\text{xiv}).$$

The electric force can thus be considered as compounded of a force ϕ_2 parallel to the axis of the oscillator, and depending only on the distance of the point of the field from its centre, and of a force $\phi_1 \sin \theta$, acting in the meridian plane perpendicular to the central distance of any point and towards the oscillator axis.



Clearly along the axis and in the equatorial plane $R = 0$, or the force is parallel to the axis, a result already deduced by HERTZ for a simple harmonic oscillation.* At very great distances we may neglect inverse squares and cubes of r , as compared with first powers, and accordingly ϕ_2 vanishes as compared with ϕ_1 . In other words the electric force tends at great distances to become perpendicular to the radius CL , or the propagation to be *purely transverse*.

At a considerable distance from the origin we may take :

* 'Electric Waves,' pp. 142-3

$$Z = \frac{El \left(\frac{2\pi}{\lambda} \right)^3 e^{-\nu(t/2\tau - r/\lambda)}}{2\pi r/\lambda} \sin^2 \theta \frac{\sin \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + 2\chi \right\}}{\cos^2 \chi},$$

$$R = - \frac{El \left(\frac{2\pi}{\lambda} \right)^3 e^{-\nu(t/2\tau - r/\lambda)}}{2\pi r/\lambda} \sin \theta \cos \theta \frac{\sin \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + 2\chi \right\}}{\cos^2 \chi} \quad \dots \quad (\text{xv}).$$

The values in our notation obtained by HERTZ are :

$$Z = \frac{El \left(\frac{\pi}{\lambda} \right)^3}{2\pi r/\lambda} \sin^2 \theta \sin 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right),$$

$$R = - \frac{El \left(\frac{2\pi}{\lambda} \right)^3}{2\pi r/\lambda} \sin \theta \cos \theta \sin 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right).$$

Now it must be remembered that Q and R and Z are all zero until t is $> ar$ or $\frac{t}{2\tau} > \frac{r}{\lambda}$. Hence HERTZ'S formulæ imply that at a considerable distance from the origin the intensity of the field increases *gradually* from zero. The formulæ (xv) appear, however, to show that the intensity at a distant point of the field rises abruptly from zero to the definite value :

$$\frac{El \left(\frac{2\pi}{\lambda} \right)^3}{2\pi r/\lambda} \sin \theta \frac{\sin 2\chi}{\cos^2 \chi} = \frac{2El \left(\frac{2\pi}{\lambda} \right)^3}{2\pi r/\lambda} \sin \theta \tan \chi$$

as the wave reaches it.

The explanation of this is, however, that, while we make the oscillator start from zero charge, yet the initiation is sudden in so far as it requires definite initial values of the electric and magnetic forces. There is an impulsive action at the wave front due to the sudden starting of the oscillator, and the above expression only represents the electric force at a considerable distance from the oscillator, when the impulsive action of the wave front has just passed the point under consideration.

Turning now to the magnetic force P perpendicular to the meridian plane, we have by (vi) :

$$P = a \frac{1}{\rho} \frac{dQ}{dt},$$

or,

$$P = \frac{El \left(\frac{2\pi}{\lambda} \right)^3 e^{-\nu(t/2\tau - r/\lambda)}}{2\pi r/\lambda} \sin \theta \left[- \frac{\sin \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + 2\chi \right\}}{\cos^2 \chi} + \frac{\cos \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \chi \right\}}{(2\pi r/\lambda) \cos \chi} \right] \quad (\text{xvi}),$$

$$= \phi_3 \sin \theta$$

where ϕ_3 is a function of r and t only, and is constant at any time for a spherical surface round the centre of the oscillator.

Clearly P does not, as in HERTZ's formula, appear to gradually rise from a zero value, but suddenly springs to the value

$$\frac{El \left(\frac{2\pi}{\lambda} \right)^3}{2\pi r/\lambda} \sin \theta \left(\frac{1}{2\pi r/\lambda} - 2 \tan \chi \right),$$

or,

$$= - \frac{2El \left(\frac{2\pi}{\lambda} \right)^3}{2\pi r/\lambda} \sin \theta \tan \chi,$$

at a considerable distance from the oscillator.* This must again be interpreted as representing the value of the magnetic force immediately after the impulsive action at the wave front has passed by.

(5.) We shall now consider what modifications are made in the velocity of transmission owing to the damping of the wave train. HERTZ, GRAY, and others have considered this problem, but have confined their attention to the equatorial plane or the axis, and to a simple harmonic train. There appears to be no real simplicity gained by these limitations. Dealing first with magnetic force in (xvi), we may write the value of P above

$$P = P_0(r) e^{-r(t/2\tau - r/\lambda)} \sin \theta \cos \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \beta_0 \right\}. \quad \dots \quad (\text{xvii})$$

where we have

$$P_0(r) \cos \beta_0 = \frac{El \left(\frac{2\pi}{\lambda} \right)^3}{2\pi r/\lambda} \left(\frac{1}{2\pi r/\lambda} - 2 \tan \chi \right),$$

$$P_0(r) \sin \beta_0 = \frac{El \left(\frac{2\pi}{\lambda} \right)^3}{2\pi r/\lambda} \left(\tan \chi \frac{1}{2\pi r/\lambda} + \frac{\cos 2\chi}{\cos^2 \chi} \right).$$

Hence

$$\left. \begin{aligned} P_0(r) &= \frac{El \left(\frac{2\pi}{\lambda} \right)^3}{(2\pi r/\lambda) \cos \chi} \left\{ 1 + \left(\frac{1}{2\pi r/\lambda} - \tan \chi \right)^2 \right\}^{\frac{1}{2}}, \\ \tan \beta_0 &= \frac{\frac{\sin \chi \cos \chi}{2\pi r/\lambda} + \cos 2\chi}{\frac{\cos^2 \chi}{2\pi r/\lambda} - \sin 2\chi} \end{aligned} \right\} \dots \quad (\text{xviii}).$$

* The apparent equality of the initial electric and magnetic forces arises from the units selected by HERTZ, which have been here adopted for purposes of comparison between the two theories. See 'Electric Waves,' pp. 138-9.

From these we deduce

$$\cot(\beta_0 - \chi) = \frac{1}{2\pi r/\lambda} - \tan \chi \quad \dots \quad (\text{xix}),$$

$$P_0(r) = \frac{El(2\pi/\lambda)^2}{(2\pi r/\lambda) \cos \chi \sin(\beta_0 - \chi)} = \frac{El(2\pi/\lambda)^2 \cos(\beta_0 - 2\chi)}{\cos^2 \chi \sin^2(\beta_0 - \chi)} \quad \dots \quad (\text{xx}).$$

From (xix)

$$\frac{1}{\sin^2(\beta_0 - \chi)} \frac{d\beta_0}{dr} = \frac{2\pi/\lambda}{(2\pi r/\lambda)^2},$$

or,

$$\frac{d\beta_0}{dr} = \frac{2\pi/\lambda}{(2\pi r/\lambda)^2} \frac{1}{\left(\frac{1}{2\pi r/\lambda} - \tan \chi\right)^2 + 1}.$$

To find the wave-speed, we have from (xvii) to find dr/dt from

$$2\pi\left(\frac{t}{2\tau} - \frac{r}{\lambda}\right) + \beta_0 = \text{constant},$$

i.e.,

$$\frac{\lambda}{2\tau} - \frac{dr}{dt} \left(1 - \frac{\lambda}{2\pi} \frac{d\beta_0}{dr}\right) = 0.$$

Let $\lambda/2\tau = v$ as before, and $dr/dt = V_0$. Then

$$V_0/v = \frac{1}{1 - \frac{\xi}{1 + (\xi - \tan \chi)^2}},$$

where $\xi = \frac{1}{2\pi r/\lambda}$. Hence

$$\frac{V_0 - v}{v} = \frac{\xi^2}{1 + \tan^2 \chi - 2\xi \tan \chi} = \frac{1}{2 \tan \chi} \times \frac{\xi^2}{\operatorname{cosec} 2\chi - \xi} \quad \dots \quad (\text{xxi}).$$

Now this result is quite independent of the *direction* of propagation, or the wave moves outwards with the same velocity at the same distance in all directions.

For $\chi = 0$, $\frac{V_0 - v}{v} = \xi^2$. This is the value given by GRAY for propagation in the equatorial plane,* but it is clearly independent of direction. At considerable distances ξ is very small, and therefore $V_0 = v$. Thus v is the limit of wave velocity as we recede from the source of disturbance.

Now a remarkable result flows from (xxi), which could not in any way be predicted from HERTZ's theory, neglecting the damping. HERTZ tells us that the velocity of propagation at the source is infinite, and GRAY draws the same conclusion, but (xxi) shows us that near the source the velocity of propagation, although very great, is

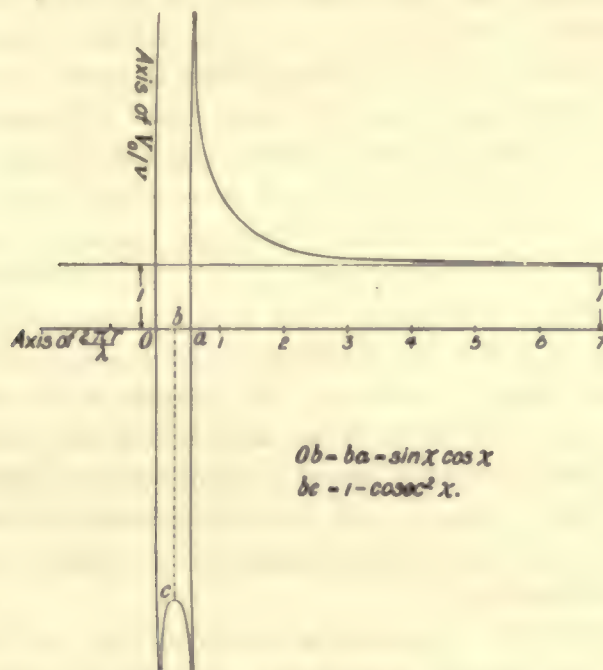
* 'Absolute Measurements,' vol. 2, p. 781

negative. This holds until $\xi = \operatorname{cosec} 2\chi$, and then V_o become indefinitely great positively. Thus, from the surface of the sphere $r = \frac{\lambda \sin 2\chi}{2\pi}$ the waves move inwards and outwards with indefinitely great velocities. When $\chi = 0$, this sphere closes in on the oscillator, and it will generally be well within the sphere round the oscillator within which it is not legitimate to apply the theory. But for a very rapidly damped wave train and a very considerable wave length, it is possible that its existence could be physically detected.

We may write (xxi)

$$\frac{V_o}{v} = 1 + \frac{\cos^2 \chi}{\frac{2\pi r}{\lambda} \left(\frac{2\pi r}{\lambda} - \sin 2\chi \right)} \quad \dots \dots \dots (\text{xxii}).$$

Hence V_o/v is symmetrical about $2\pi r/\lambda = \frac{1}{2} \sin 2\chi$, and we have the following curve for V_o/v plotted to $2\pi r/\lambda$:



N.B.— This figure is purely diagrammatic. Ob is not really comparable with $O1$, and bc is possibly 20,000 units of the vertical scale.

The diagram illustrates the rapidity with which the velocity of the magnetic disturbance approximates to v , and shows the minimum negative velocity $v \operatorname{cosec}^2 \chi$ occurring at a distance $r = \frac{\lambda}{4\pi} \sin 2\chi$ from the centre of the oscillator.

(6.) Turning now to the wave-speed for the electric force, we see from the remarks on (xiv) that we can treat the wave as made up of two components corresponding to

ϕ_1 and ϕ_2 . This is really a kinematic resolution convenient for analysis of the wave phenomena. We might have resolved the displacement in other ways, possibly with equal advantage. But it must not be supposed that a purely kinematical resolution into wave components can have no physical significance. It is true that neither ϕ_1 nor ϕ_2 could exist by themselves, but this is practically true of all the wave resolutions the mathematical physicist habitually deals with. He is accustomed to consider in electro-magnetism waves of electric and magnetic force, neither have an independent existence; of radial and transverse electric displacement, one is impossible without the other. In the theory of the refraction and reflection of waves at the interface of elastic media, and its applications to the undulatory theory of light, we do not hesitate to separate the waves of transverse from longitudinal displacement and to speak of the former as having an independent existence, yet we are really separating kinematically what can only coexist. Lastly, consider, perhaps, the most familiar case, that of the longitudinal vibrations of rods; here the physicists carry the kinematic resolution so far that they often forget to mention the coexistence of the vibrations perpendicular to the axis of the rod, without which the longitudinal vibrations could not exist at all. The fact is that a purely kinematic resolution is often of first-class physical importance, for one or other of its factors admits of ready physical determination. Thus, in our present case, ϕ_2 is the sole component of electric force in the axis of the oscillator, and determined there it is determined for all points of space at the same distance from the centre. Again, $\phi_1 + \phi_2$ is the component of electric force in the equatorial plane, and with determinations there, ϕ_2 will be known at all points of space. But it was precisely in the direction of the axis and in the equatorial plane that HERTZ made his chief experiments. Thus there seems considerable advantage in reducing the analysis of the electric force to two functions, both independent of the latitudes and varying only with the distance from the oscillator, which can be directly tested in the localities HERTZ found best suited to experimental enquiries. ϕ_1 and ϕ_2 are both independent of the latitude, and give wave speeds V_1 and V_2 having the same values for all points at the same distances from the centre of the oscillator.

The reader will notice that in taking ϕ_2 and $\phi_1 \sin \theta$ as our constituents we have resolved the electric force into two components, one along the axis and one transverse to the ray, and these components will not generally be at right angles. Neither will represent the total force in the given direction; they are transverse and axial components and not total transverse and total axial electric forces.

$$\begin{aligned} \text{The total force perpendicular to axis} &= -\phi_1 \sin \theta \cos \theta; \\ \text{The total axial electric force} &= \phi_1 \sin^2 \theta + \phi_2; \\ \text{The total transverse electric force} &= -(\phi_1 + \phi_2) \sin \theta; \text{ and} \\ \text{The total radial electric force} &= \phi_2 \cos \theta. \end{aligned}$$

It will be observed that the amplitude of the axial component does not change

with θ , but that the amplitude of both the total transverse and the total electric radial forces does. So far as the theory of wave transmission goes, the wave-speed of the total radial force is really discussed under the treatment of ϕ_2 , our axial component, in Art. 7. Similarly, the total transverse electric force has a wave-speed determined from $\phi_1 + \phi_2$ and, therefore, it will be found fully discussed under our treatment of the function $\phi_1 + \phi_2$, the equatorial wave in Art. 12. In addition, our analysis enables us to deal separately with that portion of the total transverse force ϕ_1 , or the transverse component in our case, which alone is propagated to considerable distances, and which gives at all distances the total force perpendicular to the axis.

(7.) Let us deal first with the case of the component force parallel to the axis or the ϕ_2 factor of the total radial electric force. We may write

$$\phi_2 = P_2(r) e^{-v(t/2\tau - r/\lambda)} \sin \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \beta_2 \right\} \quad \text{. (xxiii),}$$

where

$$P_2(r) \sin \beta_2 = 2El \left(\frac{2\pi}{\lambda} \right)^3 \xi^2$$

$$P_2(r) \cos \beta_2 = -2El \left(\frac{2\pi}{\lambda} \right)^3 \xi^2 (\tan \chi - \xi).$$

Thus,

$$P_2(r) = 2El \left(\frac{2\pi}{\lambda} \right)^3 \xi^2 \{ 1 + (\tan \chi - \xi)^2 \}^{\frac{1}{2}},$$

and,

$$\cot \beta_2 = -\tan \chi + \xi \quad \text{. (xxiv).}$$

Hence

$$\frac{1}{\sin^2 \beta_2} \frac{d\beta_2}{dr} = \frac{\lambda}{2\pi} \frac{1}{r^2} = \frac{2\pi}{\lambda} \xi^2,$$

and differentiating $2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \beta_2 = 0$ with regard to the time to find $V_2 = dr/dt$, we have

$$v = V_2 (1 - \xi^2 \sin^2 \beta_2).$$

Thus the wave is

$$\phi_2 = \frac{2El \left(\frac{2\pi}{\lambda} \right)^3}{(2\pi r/\lambda)^2} \left\{ 1 + \left(\tan \chi - \frac{\lambda}{2\pi r} \right)^2 \right\}^{\frac{1}{2}} e^{-v(t/2\tau - r/\lambda)} \times \sin \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \beta_2 \right\} \quad \text{(xxv),}$$

and its velocity is given by

$$V_2/v = 1 + \frac{\cos^2 \chi}{2\pi r \left(\frac{2\pi r}{\lambda} - \sin 2\chi \right)} \quad \text{. (xxvi).}$$

We see at once that $V_2 = V_0$, or the magnetic wave and the wave of component electric

force parallel to the axis are propagated everywhere with the same velocity at the same distance from the axis. At the same time the amplitude of this electric wave varies inversely as the *square* of the distance from the centre of the oscillator for considerable distances, while the amplitude of the magnetic wave varies under the same conditions inversely as the distance. Thus the effect of the former is rapidly insensible as compared with the latter. Meanwhile it is important to observe how this wave keeps pace with the magnetic wave.

(8.) We may now consider ϕ_1 , which gives the transverse electric component $\phi_1 \sin \theta$ and the total electric force perpendicular to the axis, i.e., $-\phi_1 \sin \theta \cos \theta$.*

$$\phi_1 \sin \theta = P_1(r) e^{-\nu(t/2\tau - r/\lambda)} \sin \theta \times \sin \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \beta_1 \right\} \quad (\text{xxvii}),$$

where

$$P_1(r) \cos \beta_1 = El \left(\frac{2\pi}{\lambda} \right)^3 \xi (1 - \tan^2 \chi + 3\xi \tan \chi - 3\xi^2),$$

$$P_1(r) \sin \beta_1 = El \left(\frac{2\pi}{\lambda} \right)^3 \xi (2 \tan \chi - 3\xi).$$

Hence

$$P_1(r) = \frac{El \left(\frac{2\pi}{\lambda} \right)^3 \xi}{\cos^2 \chi} \{ 1 - 3\xi \sin 2\chi + 3\xi^2 \cos^2 \chi (1 + 4 \cos^2 \chi) - 3\xi^3 \sin 2\chi \cos^2 \chi + 9\xi^4 \cos^4 \chi \} \quad (\text{xxviii}),$$

and

$$\tan \beta_1 = \frac{2 \tan \chi - 3\xi}{1 - \tan^2 \chi + 3\xi \tan \chi - 3\xi^2}.$$

From the last equation we deduce, if $\zeta = 1/\xi = \frac{2\pi r}{\lambda}$,

$$\tan (\beta_1 - 2\chi) = \frac{-3(1 + \tan^2 \chi)(\zeta - \sin 2\chi)}{\zeta^2(1 + \tan^2 \chi)^2 - 3\zeta \tan \chi(1 + \tan^2 \chi) - 3(1 - \tan^2 \chi)} = \frac{-3\epsilon}{(\epsilon + \gamma)^2 - 3(1 - \gamma^2)}$$

where

$$\epsilon = (1 + \tan^2 \chi)(\zeta - \sin 2\chi), \quad \gamma = \frac{1}{2} \tan \chi.$$

Hence

$$\frac{1}{\cos^2 (\beta_1 - 2\chi)} \frac{d\beta_1}{dr} = 3(1 + \tan^2 \chi) \frac{2\pi}{\lambda} \times \frac{3 + \epsilon^2 - 4\gamma^2}{\{(\epsilon + \gamma)^2 - 3(1 - \gamma^2)\}^2},$$

$$\frac{d\beta_1}{dr} = \frac{2\pi}{\lambda} \frac{3(1 + 4\gamma^2)(3 + \epsilon^2 - 4\gamma^2)}{(\epsilon^2 + 2\gamma\epsilon + 4\gamma^2 - 3)^2 + 9\epsilon^2}.$$

* This again is an important physical significance for ϕ_1 , and enables it to be readily differentiated physically from ϕ_2 and $\phi_1 + \phi_2$.

We must now differentiate $\frac{2\pi}{\lambda}(vt - r) + \beta_1 = 0$, to get the velocity V_1 , and we find

$$v = V_1 \left(1 - \frac{\lambda}{2\pi} \frac{d\beta_1}{dr} \right),$$

or,

$$\frac{V_1}{v} = 1 + \frac{1}{\frac{2\pi}{\lambda} \frac{1}{d\beta_1/dr} - 1}.$$

Substituting for $d\beta_1/dr$, we have, after reductions :

$$\frac{V_1}{v} = 1 + \frac{3(1 + 4\gamma^2) \{ \epsilon^2 - (4\gamma^2 - 3) \}}{\epsilon^4 + 4\gamma\epsilon^3 + 4\gamma(4\gamma^2 - 3)\epsilon + 16\gamma^2(4\gamma^2 - 3)}.$$

Now let

$$\left. \begin{aligned} \zeta_0 &= \sin 2\chi \\ \zeta_1^2 &= \cos^2 \chi (3 \cos^2 \chi - \sin^2 \chi) \end{aligned} \right\} \dots \dots \dots (\text{xxix}).$$

Then

$$\zeta_0 = \frac{4\gamma}{1 + 4\gamma^2}, \quad \zeta_1^2 = \frac{3 - 4\gamma^2}{(1 + 4\gamma^2)^2},$$

and

$$\begin{aligned} \frac{V_1}{v} &= 1 + \frac{3 \cos^2 \chi \{ (\zeta - \zeta_0)^2 + \zeta_1^2 \}}{(\zeta - \zeta_0)^4 + \zeta_0 (\zeta - \zeta_0)^3 - \zeta_0 \zeta_1^2 (\zeta - \zeta_0) - \zeta_0^2 \zeta_1^2} \\ &= 1 + 3 \cos^2 \chi \frac{\{ (\zeta - \zeta_0)^2 + \zeta_1^2 \}}{\zeta \{ (\zeta - \zeta_0)^3 - \zeta_0 \zeta_1^2 \}}. \end{aligned}$$

Let $\zeta_0 = 2\pi r_0/\lambda$, $\zeta_1 = 2\pi r_1/\lambda$. Then

$$\frac{V_1}{v} = 1 + \frac{3 \cos^2 \chi}{(2\pi/\lambda)^2} \frac{(r - r_0)^2 + r_1^2}{r \{ (r - r_0)^3 - r_0 r_1^2 \}} \dots \dots \dots (\text{xxx}).$$

This gives the velocity V_1 at each distance r from the origin of the transverse electric wave. Its amplitude is given by (xxviii).

When r is great, the amplitude approaches the value

$$\frac{El(2\pi/\lambda)^2}{\cos^2 \chi (2\pi r/\lambda)}.$$

Therefore at such distances

$$\phi_2/\phi_1 = 2(\lambda/2\pi r),$$

or ϕ_2 is insensible as compared with ϕ_1 . Even at distances 5 to 10 times the wave length, ϕ_2 will be very small as compared with ϕ_1 ; that is to say, the electric vibrations at comparatively short distances are to all intents and purposes *transverse*.

Turning now to the velocity V_1 , we will first endeavour to trace its changes. Let

us write $r_0/r_1 = q^3$, where q is generally a small quantity. Then the denominator of the expression for $V_1 - v$ in terms of r (see xxx) may be written

$$r(r - r_0 - qr_1) \{(r - r_0)^2 + (r - r_0)qr_1 + q^2r_1^2\}.$$

The second factor is negative for $r < r_0 + qr_1$, then vanishes for $r = r_0 + qr_1$, and is ever afterwards positive.

The third factor would vanish for imaginary values only, and since it is positive for $r = r_0$, it remains positive always. This supposes that r_1^2 is positive. Similarly the numerator in the value of ϕ_1 , or $(r - r_0)^2 + r_1^2$ will always be positive, if r_1^2 be positive. Now by (xxix), r_1^2 cannot be negative unless $\tan \chi > \sqrt{3}$ or $\chi > 60^\circ$. This corresponds to a degree of damping in which the amplitude would be reduced to '000019 of itself every period, or a degree immensely higher than that of the usual Hertzian oscillator. Hence both the numerator and the third factor of the denominator are always positive.

Accordingly $V_1 - v$ is negatively infinite for $r = 0$, becomes negatively finite, but very large, until $r = r_0 + qr_1$ when it again becomes negatively infinite, after this it becomes positively infinite, and rapidly decreases to zero as r increases. Thus, as in the case of the other waves, there is a sphere round the oscillator within which the waves move inwards for transverse electric vibrations. This sphere is of somewhat larger radius ($r_0 + qr_1$ as compared with r_0) than in the case of the magnetic wave. In terms of χ the radius of this sphere is given by

$$\frac{\lambda}{2\pi} (\sin 2\chi) \left\{ \left(\frac{3}{4} \operatorname{cosec}^2 \chi - 1 \right)^{1/3} + 1 \right\}.$$

For example, when $\tan \chi = 2/\pi$ or $\chi = 3^\circ 38' 33'' \cdot 5$, we find for the radius of this sphere, $6 \cdot 69604 r_0$, or between six and seven times the radius of the sphere within which the velocity of the magnetic wave is negative. Substituting the value of r_0 , the radius = $\cdot 135\lambda$. Hence, for a small oscillator, say $\frac{1}{10}$ of a wave-length long, this sphere would be well outside the sphere $\cdot 05$ of a wave-length circumscribing the oscillator, and thus practically within the field to which our theory might be approximately applied. The inward moving wave of transverse electric vibrations ought thus to be capable of experimental demonstration.

We have, in the next place, to find the minimum negative velocity, and its distance from the centre.

Writing $r - r_0 = u$ and $r_0 = q^3r_1$, we have to find the maxima or minima of

$$\frac{u^2 + r_1^2}{(u + q^3r_1)(u^3 - q^3r_1^3)}.$$

Differentiating, we find for the required values

$$2\left(\frac{u}{r_1}\right)^5 + q^3\left(\frac{u}{r_1}\right)^4 + 4\left(\frac{u}{r_1}\right)^3 + 4q^3\left(\frac{u}{r_1}\right)^2 + 2q^6\left(\frac{u}{r_1}\right) - q^3 = 0 \quad \text{(xxxix)}.$$

Now, at $r = r_0$ it is easy to see that the curve in which $\frac{V_1 - v}{v}$ is plotted to r is still sloping towards the horizontal. For if $\frac{V_1 - v}{v} = \eta$ and $r - r_0 = \xi$, its equation is approximately

$$\eta = - \frac{3 \cos^2 \chi}{(2\pi/\lambda)^2} \frac{1}{r_0 (r_0 + \xi)},$$

or, η decreases with increase of ξ hyperbolically.

Hence the minimum negative value sought must lie between r_0 and $r_0 + qr_1$, say at $r_0 + \eta qr_1$, where η is less than unity but not necessarily very small. Thus we must put $u/r_1 = \eta q$, where q is small, and endeavour to solve (xxx). Substituting, we have

$$2q^5\eta^5 + q^7\eta^4 + 4q^3\eta^3 + 4q^5\eta^2 + 2q^7\eta - q^3 = 0,$$

or,

$$2q^2\eta^5 + q^4\eta^4 + 4\eta^3 + 4q^2\eta^2 + 2q^4\eta - 1 = 0.$$

Clearly, η must be of the form $\eta_0 + \eta_1 q^2 + \eta_2 q^4 + \eta_3 q^6 + \&c.$ Let us substitute this value and equate the successive powers of q^2 as well as the constant term to zero. We find

$$4\eta_0^3 - 1 = 0,$$

$$\eta_0^5 + 6\eta_1\eta_0^2 + 2\eta_0^2 = 0,$$

$$10\eta_0^4\eta_1 + \eta_0^4 + 12\eta_0^2\eta_2 + 12\eta_0\eta_1^2 + 8\eta_0\eta_1 + 2\eta_0 = 0,$$

$$10\eta_0^4\eta_2 + 20\eta_0^3\eta_1^2 + 4\eta_0^3\eta_1 + 12\eta_0^2\eta_3 + 24\eta_0\eta_1\eta_2 + 4\eta_1^3 + 8\eta_0\eta_2 + 4\eta_1^2 + 2\eta_1 = 0.$$

These equations give us

$$\begin{array}{l} \eta_0 = (\frac{1}{4})^{1/3} = \cdot 62996 \\ \eta_1 = -\frac{3}{8} = -\cdot 375 \\ \eta_2 = 0 \\ \eta_3 = \cdot 01476 \end{array} \quad \dots \dots \dots (xxxii).$$

Thus

$$\eta = \cdot 62996 - \cdot 375q^2 + \cdot 01476q^4.$$

We find at once that the required radius of the sphere at which the velocity of the electric transverse wave takes a minimum negative value

$$\begin{aligned} &= r_0 + \eta qr_1 = r_0 (1 + \eta/q^2) \\ &= r_0 \left(\frac{\cdot 62996}{q^2} + \cdot 625 + \cdot 01476q^4 \right) \dots \dots \dots (xxxiii). \end{aligned}$$

The next term in the expression for the radius would involve q^6 and may generally be neglected. If the point of minimum velocity were half-way between the two

points of infinite negative velocity, we should have the radius $= \frac{1}{2}(r_0 + qr_1)$
 $= r_0 \left(\frac{5}{q^2} + \cdot 5 \right)$. Hence, the point of minimum velocity is more than half-way
 towards the outer point of infinite velocity. For the particular oscillator referred to on
 p. 162, $q^2 = \cdot 17556$, and the radius of the sphere of minimum velocity $= 4\cdot 21 r_0$ nearly,
 while the sphere of infinite negative velocity has $6\cdot 70 r_0$ for radius nearly (see p. 174).

At a distance from the centre of the oscillator we have very approximately

$$\frac{V_1 - v}{v} = \frac{3 \cos^2 \chi}{(2\pi r/\lambda)^2},$$

or,

$$V_1 - v = 3(V_2 - v).$$

Thus at some distance from the centre of the oscillator, the excess of the velocity
 of this component transverse electric wave (or of the total electric wave perpendicular
 to the axis) over the velocity of light is three times the excess of the velocity of the
 magnetic wave.

In order to find the distance from the centre at which this component transverse
 electric and the magnetic waves have equal negative velocities we must make

$$\frac{1}{r(r-r_0)} = \frac{3\{(r-r_0)^2 + r_1^2\}}{r\{(r-r_0)^3 - r_0 r_1^2\}},$$

or, putting $r - r_0 = u$, solve the cubic

$$2u^3 + 3r_1^2 u + r_0 r_1^2 = 0.$$

Take $u = -\eta r_0 = -\eta q^2 r_1$; hence

$$2\eta^3 q^6 + 3\eta - 1 = 0.$$

Thus,

$$\eta = \frac{1}{3} - \frac{2}{81} q^6, \text{ nearly } \dots \dots \dots (\text{xxxiv}).$$

We conclude accordingly that the two velocities are negatively equal at a distance
 from the centre equal to $\frac{2}{3}r_0(1 + \frac{1}{27}q^6) = \frac{2}{3}r_0$, nearly.

This equal negative velocity is $v\left(1 - \frac{1\cdot 125}{\sin^2 \chi}\right)$, nearly. Similarly, the minimum
 negative velocity of the electric transverse wave may be shown to be

$$v\left\{1 - \frac{1\cdot 58740 q^2}{\sin^2 \chi}(1 - 1\cdot 19055 q^2 + 2\cdot 12601 q^4)\right\} \dots \dots \dots (\text{xxxv}),$$

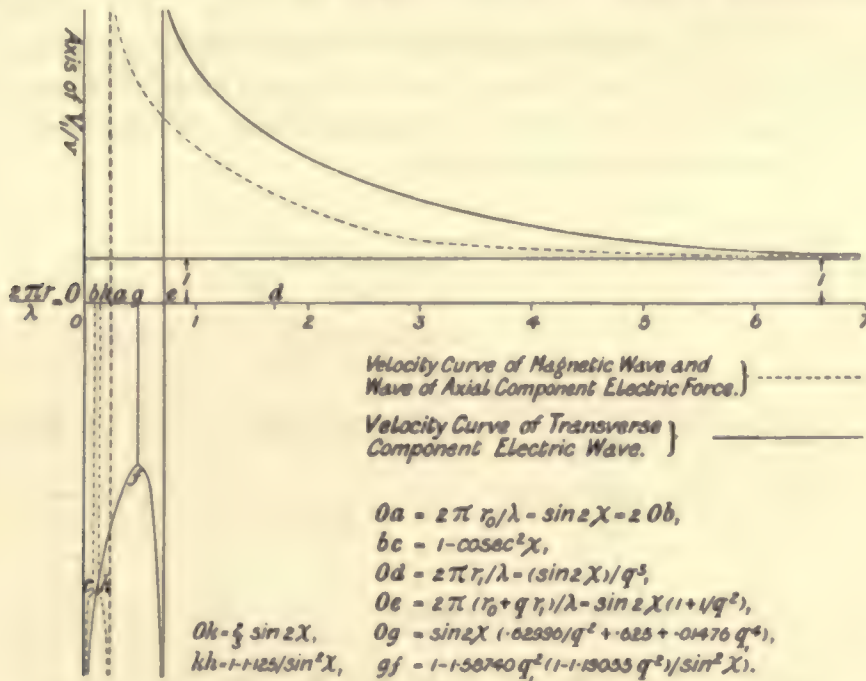
where $q^2 = \frac{1}{\{\frac{3}{4} \operatorname{cosec}^2 \chi - 1\}^{1/3}}$ as before.

For the special oscillator discussed above it equals $-59\cdot 545$, or is slightly less
 than 60 times the velocity of light. The minimum negative velocity of the trans-

verse magnetic wave = $-248.46v$, and the equal negative velocity of both waves = $-279.64v$. Thus again it appears more feasible to test experimentally the negative velocity of this transverse electric wave than that of the magnetic wave.

With regard to these negative waves, we can only cite what HERTZ has remarked on the infinite motion which occurs with a steady oscillator ('Electric Waves,' p. 146): "At an infinitesimal distance from the origin the velocity of propagation is even infinite. This is the phenomenon which, according to the old mode of expression, is represented by the statement that upon the electromagnetic action, which travels with velocity $1/A$ [our v], there is superposed an electrostatic force travelling with infinite velocity. In the sense of our theory we more correctly represent the phenomenon by saying that fundamentally the waves which are being developed do not owe their formation solely to processes at the origin, but arise out of the conditions of the whole of the surrounding space, which latter, according to our theory, is the true seat of the energy."

The following figure gives the velocity curve of the transverse component electric wave or of the total electric wave perpendicular to the axis *diagrammatically*.



(9.) It is noteworthy that HERTZ, speaking of the electric force in the equatorial plane, i.e.,

$$Z = \phi_1 + \phi_2,$$

says that it cannot *possibly* be broken up into two simple waves travelling with different velocities ('Electric Waves,' p. 151). The explanation of HERTZ's difficulty is, perhaps, simple; for, having put $\theta = \pi/2$, the distinction between ϕ_1 and ϕ_2 was

lost in his theory. We may consider these to be two separate waves travelling in the equatorial plane, both indeed transverse just for this plane, but one ϕ_1 travelling with the velocity of the transverse component electric wave and the other with the velocity of the magnetic wave, or that of the wave of axial component electric force. Thus HERTZ's original explanation of the irregularity of the interferences which did not succeed each other at equal distances, but with more rapid changes in the neighbourhood of the oscillator, seems justified by the fuller theory. Namely, he explained this behaviour by the supposition "that the total force might be split up into two parts, of which the one, the electromagnetic, was propagated with the velocity of light, while the other, the electrostatic, was propagated with greater and perhaps infinite velocity." Actually we may resolve into two waves; the transverse component electric wave is propagated with greater velocity than the wave of axial component electric force, which has the velocity of the magnetic wave. Many of HERTZ's experiments were made at a comparatively short distance from the oscillator, and some of the discrepancies he noted between his theory and experiment seem capable of explanation by aid of the velocity diagram given above.

(10.) There is another quantity which HERTZ considers at length, namely, the rate of change of the magnetic force, which gives the integral force of induction round a small circle in a plane perpendicular to the magnetic force. We shall now accordingly consider the expression for dP/dt from (xvii):

$$\begin{aligned} \frac{dP}{dt} &= P_0(r) \sin \theta e^{-\nu(t/2\tau - r/\lambda)} \left\{ -p_1 \cos \left(2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \beta_0 \right) \right. \\ &\quad \left. - p_2 \sin \left(2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \beta_0 \right) \right\} \\ &= - \frac{P_0(r) v (2\pi/\lambda) \sin \theta}{\cos \chi} e^{-\nu(t/2\tau - r/\lambda)} \sin \left(2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \beta_0 + \chi \right) \\ &= - \frac{P_0(r) v (2\pi/\lambda) \sin \theta}{\cos \chi} e^{-\nu(t/2\tau - r/\lambda)} \sin \left(2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \beta_3 \right) . \quad (\text{xxxvi}), \end{aligned}$$

where $\beta_3 = \beta_0 + \chi$, and therefore from (xix),

$$\cot(\beta_3 - 2\chi) = \frac{1}{2\pi r/\lambda} - \tan \chi.$$

A more convenient form is easily deduced, namely:

$$\tan(\beta_3 - 3\chi) = \frac{2\pi}{\lambda} \left(r - \frac{1}{2} r_0 \right) / \cos^2 \chi \quad . \quad . \quad . \quad (\text{xxxvii}),$$

where $r_0 = \frac{\lambda}{2\pi} \sin \chi$ as before.

Now let δ_3 give the phase of the sine term in (xxxvi), or :

$$\delta_1 = \frac{2\pi r}{\lambda} - \beta_1.$$

Comparing with (xxiv), we see $\beta_3 = \beta_2 + 2\chi$, or :

$$\delta_1 = \delta_2 - 2\chi.$$

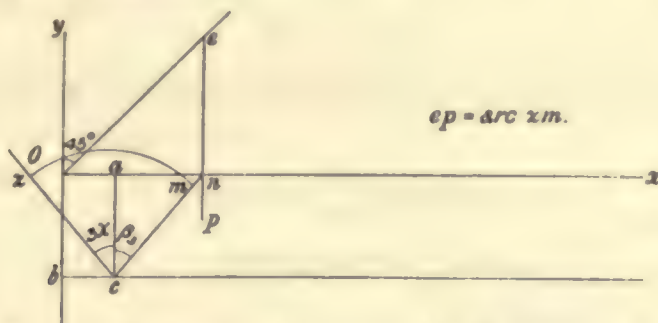
Thus the phase of the wave of magnetic induction always differs by a constant from that of the wave of axial component electric force.

Since $d\beta_1/dr = d\beta_2/dr$, the velocity of the wave of magnetic induction equals that of the wave of axial component electric force, and is given by the V_2 of (xxvi), or the diagram of p. 169.

(11.) In our diagram (p. 184) we have plotted δ_s from the calculated curve for δ_s , but it is interesting to note the following graphical construction for finding it directly. Let $\zeta = 2\pi r/\lambda$ as before.

Let Ox be the axis of ζ , Oy of δ_3 , then $\delta_3 = \zeta - \beta_3$. Take $Ob = \cos^2 \chi$, $Oa = \frac{1}{2}(2\pi r_0/\lambda) = \frac{1}{2}\zeta_0$, and let the vertical through a meet the horizontal through b in c . Let On equal ζ , then $an = \zeta - \frac{1}{2}\zeta_0$ and $an/cn = (\zeta - \frac{1}{2}\zeta_0)/\cos^2 \chi = \tan(\beta_3 - 3\chi)$, or the $\angle acn = \beta_3 - 3\chi$.

Take cz , so that $\angle zca = 3\chi$, then $\beta_3 = \angle zen$. If a circle be described round c with radius $cz = 1$, the arc zm corresponding to the angle zen is the required length β_3 . Subtract this arc (rectified, say, by RANKINE'S rule) from the corresponding ordinate ne of the 45° line through the origin ($\delta = \zeta$), and we find the true value of $\delta_3 = np$. This construction was actually gone through and compared with the calculated values for verification.



N.B.—The angle χ has been much exaggerated for diagrammatic purposes.

(12.) Before we refer the reader to our diagram giving the phases of the various waves, and describe how they were obtained, it seems well to consider the combined wave of total transverse electrical force in the equatorial plane. The resultant electrical force in this plane may be considered, as we have already seen, to consist of two parts, having different wave-speeds; but, possibly, if a receiver were sufficiently small, it might not be possible to differentiate them, and HERTZ's theoretical view of their

unity seems finally to have mastered his experimental suspicion as to the possible coexistence of two waves in this plane (see our p. 177). Accordingly we have worked out both the velocity and phase of this compound wave, which at the same time determines the total transverse wave (see p. 170), in order that a comparison may be made with HERTZ'S results for an undamped single wave in the equatorial plane.

Returning to the formula (x) and putting $\theta = \frac{1}{2}\pi$, it may be read as :

$$Z = Z_0(r) e^{-r(\frac{2\pi}{\lambda} - r)} \sin \left\{ 2\pi \left(\frac{t}{2\tau} - \frac{r}{\lambda} \right) + \beta_4 \right\} \quad \dots \quad (\text{xxxviii}),$$

where if $\xi = \frac{1}{2\pi r/\lambda}$:

$$Z_0(r) \sin \beta_4 = (2 \tan \chi - \xi) \text{El} (2\pi/\lambda)^3 \xi,$$

$$Z_0(r) \cos \beta_4 = (1 - \tan^2 \chi + \xi \tan \chi - \xi^2) \text{El} (2\pi/\lambda)^3 \xi.$$

Hence,

$$\tan \beta_4 = (2 \tan \chi - \xi) / (1 - \tan^2 \chi + \xi \tan \chi - \xi^2) \quad \dots \quad (\text{xxxix}).$$

From this we deduce :

$$\begin{aligned} \tan (\beta_4 - 2\chi) &= \frac{-\cos^2 \chi \left(\frac{2\pi r}{\lambda} - \sin 2\chi \right)}{\left(\frac{2\pi r}{\lambda} - \frac{1}{4} \sin 2\chi \right)^2 - \cos^2 \chi (\cos^2 \chi - \frac{3}{4} \sin^2 \chi)} \\ &= \frac{-c_0 (\xi - \xi_0)}{(\xi - \frac{1}{4} \xi_0)^2 - c_1^2} \quad \dots \quad (\text{xl}), \end{aligned}$$

where

$$c_0 = \cos^2 \chi, \quad \xi_0 = \sin 2\chi, \quad c_1^2 = \cos^2 \chi (\cos^2 \chi - \frac{3}{4} \sin^2 \chi).$$

This formula is fairly well adapted for logarithmic calculation. The phase may be obtained by taking

$$\delta_4 = \zeta - \beta_4.$$

It may be compared with the value for δ_1 , obtained from β_1 , on p. 172, where we easily find

$$\begin{aligned} \tan (\beta_1 - 2\chi) &= \frac{-3 \cos^2 \chi \left(\frac{2\pi r}{\lambda} - \sin 2\chi \right)}{\left(\frac{2\pi r}{\lambda} - \frac{3}{4} \sin 2\chi \right)^2 - 3 \cos^2 \chi (\cos^2 \chi - \frac{1}{4} \sin^2 \chi)} \\ &= \frac{-3c_0 (\xi - \xi_0)}{(\xi - \frac{3}{4} \xi_0)^2 - c_2^2} \quad \dots \quad (\text{xli}), \end{aligned}$$

if

$$c_2^2 = 3 \cos^2 \chi (\cos^2 \chi - \frac{1}{4} \sin^2 \chi).$$

As before

$$\delta_1 = \zeta - \beta_1.$$

This again readily lends itself to logarithmic calculation.

Both have for asymptote the same 45° line, namely,

$$\delta = \zeta - (\pi + 2\chi).$$

We now proceed to trace the velocity of the electrical disturbance in the equatorial plane.

We have

$$\tan \beta_i = \frac{2 \tan \chi - \xi}{1 - \tan^2 \chi + \xi \tan \chi - \xi^2},$$

whence, by differentiation, we find

$$\frac{\lambda}{2\pi} \frac{d\beta_i}{dr} = \frac{\xi^2 \{1 + \tan^2 \chi - 4\xi \tan \chi + \xi^2\}}{(1 + \tan^2 \chi)^2 - 2\xi \tan \chi (1 + \tan^2 \chi) - \xi^2 (1 - 3 \tan^2 \chi) - 2\xi^3 \tan \chi + \xi^4}.$$

Hence, if V_i be the velocity and $v = \lambda/(2\pi)$, as before

$$\begin{aligned} \frac{V_i}{v} &= 1 + \frac{(\lambda/2\pi) \cdot (d\beta_i/dr)}{1 - (\lambda/2\pi) \cdot (d\beta_i/dr)} \\ &= 1 + \frac{\xi^2 (1 + \tan^2 \chi - 4\xi \tan \chi + \xi^2)}{(1 + \tan^2 \chi)^2 - 2\xi \tan \chi (1 + \tan^2 \chi) - 2\xi^2 (1 - \tan^2 \chi) + 2\xi^3 \tan \chi}. \end{aligned}$$

Now put

$$\zeta = 1/\xi = 2\pi r/\lambda,$$

$$\frac{V_i}{v} = 1 + \frac{\cos^2 \chi \left\{ \left(\zeta - \frac{2 \tan \chi}{1 + \tan^2 \chi} \right)^2 + \frac{1 - 3 \tan^2 \chi}{(1 + \tan^2 \chi)^2} \right\}}{\zeta \left\{ \zeta^2 - \zeta^2 \frac{2 \tan^2 \chi}{1 + \tan^2 \chi} - 2\zeta \frac{1 - \tan^2 \chi}{(1 + \tan^2 \chi)^2} + \frac{2 \tan \chi}{(1 + \tan^2 \chi)^2} \right\}}.$$

Again put

$$\zeta_0 = \frac{2 \tan \chi}{1 + \tan^2 \chi} = \sin^2 \chi = \frac{2\pi}{\lambda} r_0,$$

$$\zeta_2^2 = \frac{1 - 3 \tan^2 \chi}{(1 + \tan^2 \chi)^2} = \cos^2 \chi (\cos^2 \chi - 3 \sin^2 \chi) = \frac{4\pi^2}{\lambda^2} r_2^2.$$

Then

$$\zeta_0^2 + \zeta_2^2 = \cos^2 \chi, \quad \zeta_0 (\zeta_0^2 + \zeta_2^2) = 2 \tan \chi / (1 + \tan^2 \chi)^2,$$

$$\zeta_2^2 + \frac{1}{2} \zeta_0^2 = \cos^2 \chi (\cos^2 \chi - \sin^2 \chi) = (1 - \tan^2 \chi) / (1 + \tan^2 \chi)^2.$$

Thus we may write the above result

$$\begin{aligned} \frac{V_i}{v} &= 1 + \frac{\cos^2 \chi \{(\zeta - \zeta_0)^2 + \zeta_2^2\}}{\zeta \{ \zeta^2 - \zeta_0 \zeta^2 - (\zeta_0^2 + 2\zeta_2^2) \zeta + \zeta_0 (\zeta_0^2 + \zeta_2^2) \}} \\ &= 1 + \frac{\cos^2 \chi \{(\zeta - \zeta_0)^2 + \zeta_2^2\}}{\zeta \{ (\zeta - \zeta_0)^2 (\zeta + \zeta_0) - 2\zeta_2^2 (\zeta - \zeta_0) - \zeta_2^2 \zeta_0 \}} \\ &= 1 + \frac{\cos^2 \chi \{ (r - r_0)^2 + r_2^2 \}}{(2\pi/\lambda)^2 r \{ (r - r_0)^2 (r + r_0) - 2r_2^2 (r - r_0) - r_2^2 r_0 \}} \quad \dots \quad (\text{xlii}). \end{aligned}$$

This is a form directly comparable with (xxx).

If the wave be not damped, $\zeta_0 = 0$, $\zeta_2 = 1$, which gives

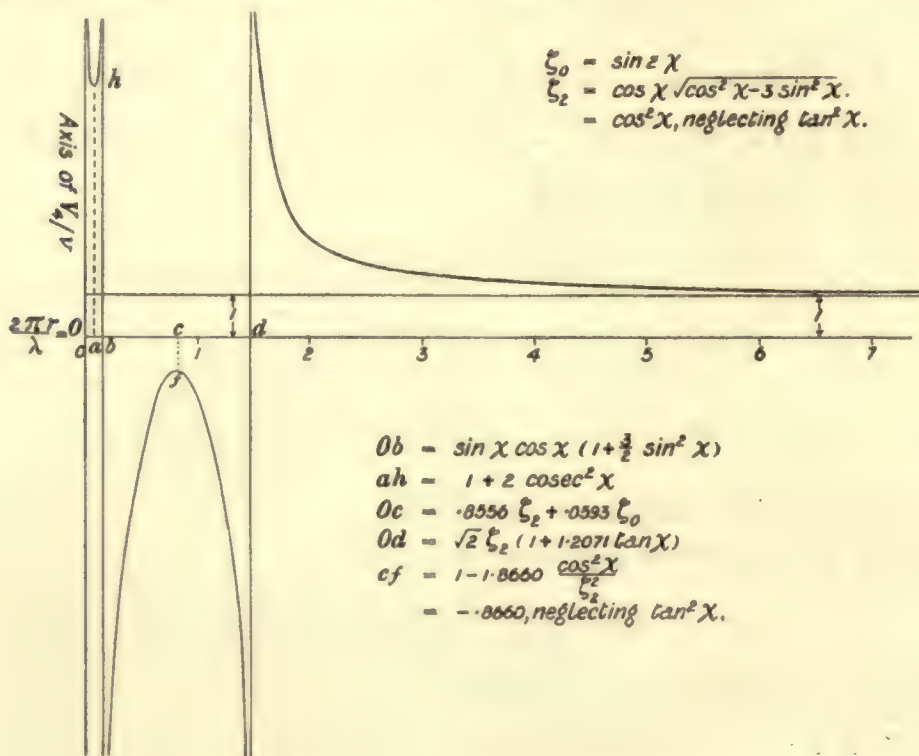
$$\frac{V_i}{v} = 1 + \frac{1 + \zeta^2}{\zeta(\zeta^2 - 2\zeta)} = \frac{1 - \zeta^2 + \zeta^4}{\zeta^2(\zeta^2 - 2)},$$

a value identical with that given by GRAY.*

* 'Absolute Measurements,' vol. 2, Part II.,

The curve giving the velocity of this wave is found to be even more complex than that for either the wave of transverse or of axial component electric force alone (p. 177). In the neighbourhood of the origin the wave starts with infinite positive velocity; this falls to a finite but very great positive velocity at about $\frac{1}{4} \zeta_0$, and then rises again and becomes infinite at about $\frac{1}{2} \zeta_0$. Beyond this we have a region of negative velocity, starting with an infinite negative velocity, and falling to a velocity even less than that of light at about $\cdot 8556 \zeta_2$. Then the velocity increases again, becoming infinite at about $\sqrt{2} \zeta_2$, after which it takes an infinite positive value and falls rapidly till it becomes equal to the velocity of light. Thus there are two centres, one at about $\frac{1}{2} \zeta_0$, and another at about $\sqrt{2} \zeta_2$ from the oscillator (more exact values are given below), from or towards which the waves appear to move with varying velocities. In most cases the $\frac{1}{2} \zeta_0$ centre would be far too near the oscillator for experiment, but the $\sqrt{2} \zeta_2$ centre, and even the point of negative velocity less than that of light, appear to be well within the field of experiment, and actually within the area inside which HERTZ made a good many experiments. Considering the complex character of the velocity of this wave of electrical disturbance in the equatorial plane, we feel doubtful as to what interpretation can possibly be put on HERTZ's interference experiments in this plane, especially on those made at a moderate distance from the oscillator.

The following figure gives the velocity curve of the equatorial electric wave *diagrammatically*. The approximate values of the chief quantities concerned have been calculated in the same manner as those on pp. 173-176, but it does not seem necessary to reproduce the calculations.



Now it is clear, both from this diagram and from that on p. 177, that we must go to $\frac{2\pi r}{\lambda} = 6$ about to get fairly constant velocity of transmission. But λ in HERTZ's experiments was about 9.6 metres (see p. 162), or the experiments, supposing a constant velocity of transmission desirable, ought to have been made at some 9 metres or more from the oscillator. HERTZ's first series are at less than 8, his third series at less than 4, and his second, which do go up to 12, he states "required rather an effort,"* Within these limits the exact nature of the interference and the points at which it may be expected to occur seem open to some criticism, even in addition to the difficulties which have been raised by the problem of "multiple resonance."† The views expressed above will be strengthened by an examination of the diagram giving the phases of the waves, the velocities of which have been already discussed.

(13.) The phases have been plotted from the formulæ given above, as follows :—

I. *Transverse Component Electric Wave and Wave of Total Force perpendicular to Axis* (ϕ_1). $\delta_1 = \zeta - \beta_1$.

The formula is (xli). For the special oscillator for which our results are plotted,

$$\begin{aligned}\zeta_0 &= \sin 2\chi = .126,8098, & c_0 &= .995,964, \\ \chi &= .063,5760, & c_2^2 &= 2.972,821.\end{aligned}$$

The asymptote is $\delta_1 = \zeta - 3.2687$ (i.e., $\delta_1 = \zeta - (\pi + 2\chi)$).

We see from the diagram that the phase does not approach very rapidly to its asymptotic value, being still about 5 per cent. of its value from it, when $\zeta = 10$.

We notice that δ_1 starts from zero at the origin, and after high contact becomes small and negative. This negative portion of the phase is too small to be seen on the large diagram, but an enlarged inset figure is added. The curve cuts the axis and becomes positive at about 1.165, or at about 1.42 metres from the origin, a distance within which some of HERTZ's experiments on interference were made. The range of negative phase could be considerably increased with a more rapidly damped oscillator.

The approximate value‡ of Oa for any value of χ is

$$= (15 \tan \chi)^{\frac{1}{2}} + \frac{20}{7} \tan \chi + \frac{2000}{1176} \tan \chi \left(\frac{\tan^2 \chi}{15} \right)^{\frac{1}{2}} + \dots \dots \dots \text{(xliii).}$$

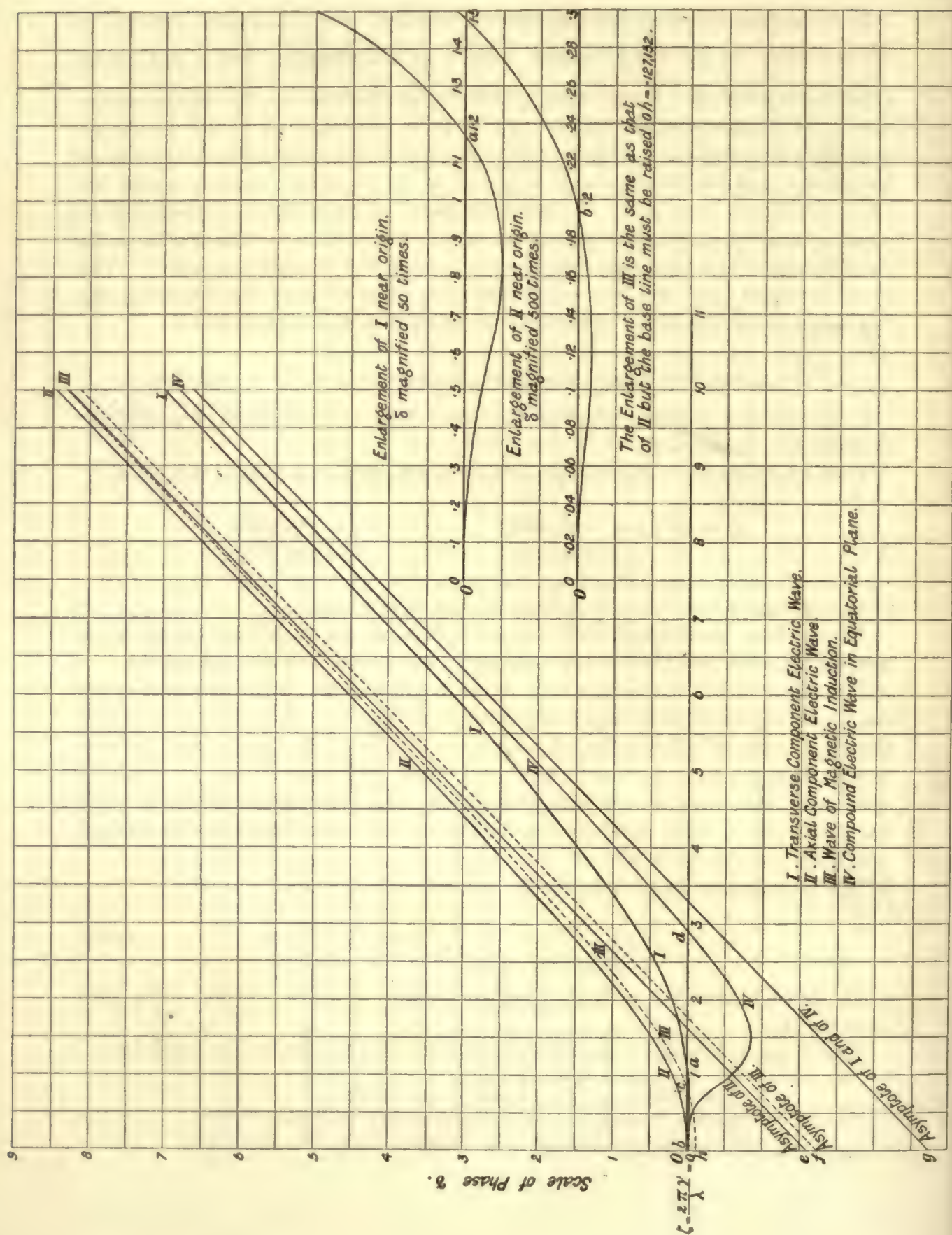
II. *Axial Component Electric Wave and Wave of Total Radial Force* (ϕ_2). $\delta_2 = \zeta - \beta_2$.

In this case the formula used was deduced from (xxiv). This may be altered to

* 'Electric Waves,' pp. 118, 120, and 119 respectively.

† POINCARÉ, 'Électricité et Optique,' vol. 2, p. 195 *et seq.*, and p. 249 *et seq.*

‡ We owe this general solution to the kindness of Mr. L. N. G. FILON, M.A.



$$\tan (\beta_2 - \chi) = \frac{\zeta - \frac{1}{2}\zeta_0}{\cos^2 \chi} \quad (\text{xliv}),$$

which serves readily for logarithmic calculation.

The portion of the curve for which δ is negative now lies between 0 and .2, and we must multiply it some 500 times to render the small negative values of δ visible.

The approximate value of Ob for any value of χ is given by

$$Ob = \frac{3}{2}\zeta_0,$$

and thus = .19021 for our special case.

The asymptote is given by the 45° line

$$\delta = \zeta - \left(\frac{\pi}{2} + \chi \right),$$

or, for our special case $Oe = 1.63437$.

The curve for this wave has a far less sensible negative portion, and approaches much more rapidly to its asymptote, being in our special case at a distance less than 2 per cent. of the value of δ from its asymptote when $\zeta = 10$.

Thus we see that there is a marked difference between the phases of the component transverse and component axial electric waves. The first appears to proceed from a centre at distance Oa given by (xliii) from the centre, and the second from a distance Ob equal $\frac{3}{2}\zeta_0$, or practically from a point so close to the centre of the oscillator as not to be sensible in the case of any but very rapidly damped wave trains. The ultimate phase difference of the two waves = $\frac{\pi}{2} + \chi$.

III. *Wave of Magnetic Induction.* $\delta_3 = \zeta - \beta_3$.

Here we can either use the graphical method of p. 179, or the simple relation $\delta_3 = \delta_2 - 2\chi$.

The latter method shows us that the asymptote is

$$\delta = \zeta - \left(\frac{\pi}{2} + 3\chi \right),$$

or in our special case

$$\delta = \zeta - 1.7615.$$

Thus the ultimate difference of phase between the transverse component electric and the magnetic waves is $\frac{1}{2}\pi - \chi$, and between the axial electric and magnetic waves is -2χ .

It will be seen that this wave of magnetic induction for a damped wave differs considerably from that given by HERTZ.

The most notable difference is the *finite negative* value of δ_3 at the origin, and this

negative value of the phase continues until $\frac{2\pi r}{\lambda} = 0c$; for the general case we may take approximately

$$0c^* = (6\chi)^{\frac{1}{3}}(1 + \frac{1}{15}(6\chi)^{\frac{1}{3}}).$$

For the special value of χ used above, i.e., $\chi = 3^\circ 38' 33.5''$, we find

$$0c = .8664.$$

This is at a distance from the source of

$$r = .1379\lambda,$$

or about 1.324 metres. Thus we see that the phase of this action does not, as HERTZ states ('Electric Waves,' p. 154), "increase continuously from the origin itself." In discussing the velocity we have seen that $d\beta_2/dr = d\beta_0/dr$, so that the velocity of propagation is identical with that given by (xxi). Thus it becomes indefinitely great when $2\pi r/\lambda = \sin 2\chi = .1268$ for the above values of the constants. The point, therefore, of infinitely great velocity is much closer to the origin than that of zero phase. We think HERTZ considered these two points to be identical. At any rate, he held that the wave moved with infinite velocity up to the point of zero phase. For he argues from his conclusion that the phase increases continuously from the origin that :

"The phenomena which point to a finite rate of propagation must in the case of these interferences† make themselves felt even close to the oscillator. This was indeed apparent in the experiments, and therein lay the advantage of this kind of interference. But, contrary to the experiment, the apparent velocity near to the oscillator comes out greater than at a distance from it"‡

As a matter of fact, the alterations in the velocity of transmission of either magnetic wave or transverse component electric wave are very complex in the neighbourhood of the oscillator, and these variations do not bear a simple relation to the points of zero phase, from which points HERTZ assumes the outward moving wave to start. Something of the difficulties HERTZ met with in his experiments on "interferences of the second kind" made close to the oscillator may well have been due to this complexity of result arising from the use of a damped wave-train.

IV. *The Compound Electric Wave in the Equatorial Plane, and the Wave of Total Transverse Electric Force* ($\phi_1 + \phi_2$). $\delta_4 = \zeta - \beta_4$.

The formula is now (xl).

For the special oscillator for which our curve is drawn, $c_0 = .995,9635$, $c_1^2 = .988,928$, $\zeta_0 = .126,8098$, and the asymptote is $\delta = \zeta - 3.2687$.

* This must only be taken as the basis to find a second approximation, as the series converges slowly.

† Interferences of the "second kind": see 'Electric Waves,' p. 119.

‡ 'Electric Waves,' p. 154.

The general value for Od , giving the point of zero phase, is $Od = 2.743,707 + .112,193 \zeta_0$, approximately. For our special case, $Od = 2.9079$.

It will be seen that our curve approaches closer to its asymptote than the curve for the true wave of transverse vibrations. Further, the centre, d , from which the wave with positive velocity may be supposed to start, is moved far further from the origin. It is rather further from the origin than it would be in the case of an undamped train.* There seems, therefore, considerable doubt as to what HERTZ was really measuring in the case of his interference experiments in the equatorial plane. Was he really measuring IV., or possibly I., obscured in its effect by the superposition of II.? It is, we think, needful to re-examine the whole matter physically, endeavouring to distinguish between the components ϕ_1 and ϕ_2 . For this purpose the direction of the axis, rather than the plane of the equator, seems the more suitable for experiment. For in this direction the magnetic induction and the transverse electric component wave disappear, and we have the axial component electric wave only to deal with, i.e., II. only, I. and III. being not extant.

Further, the numerous theoretical singular points to which we have referred seem to deserve, if possible, physical investigation. To do this we require to emphasise as much as possible their distance from the oscillator. But this means that we must get from a small oscillator a long wave-length, if the rate of damping (χ) be fixed, or, if the wave-length be fixed, we require very rapid damping. Neither of these conditions seem easy of physical realisation. Still something might be done by way of striking a balance, and, at any rate, we must not disregard the fact that a considerable portion of HERTZ's experiments were made inside that portion of the field where the influence of these singular points and of the damping should at least theoretically make themselves felt.

(14.) *Conclusions.*—We may draw the following general conclusions:—

(i.) The effect of damping makes itself very sensible in modifying the form of the wave-surface as propagated into space from a theoretical oscillator. The typical Hertzian wave-diagrams require to be replaced by the fuller series accompanying this memoir.

(ii.) *Three* waves of electro-magnetic force may be considered as sent out from the oscillator, and these waves we believe capable of physical identification.

First, a component wave of transverse electric force, determined by ϕ_1 . This also gives the wave-speed and phase of force perpendicular to the oscillator axis. Secondly, a component wave of electric force parallel to the axis, determined by ϕ_2 . This also gives the wave-speed and phase of force radial to the oscillator.

Thirdly, a wave of magnetic force.

* In this case $Od = 2.743,707$ correct to the last place. In the general approximate value given above, we have neglected terms of the order χ^2 , and the approximation is not nearly as accurate as this.

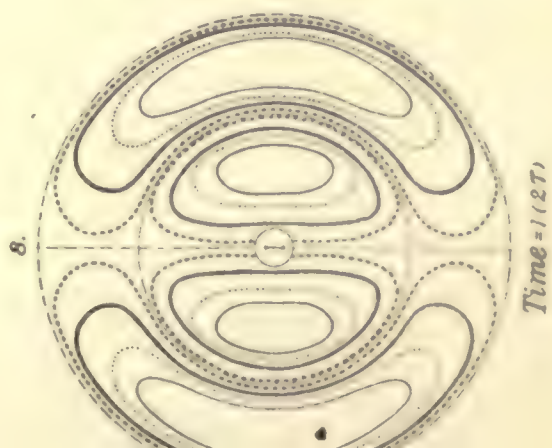
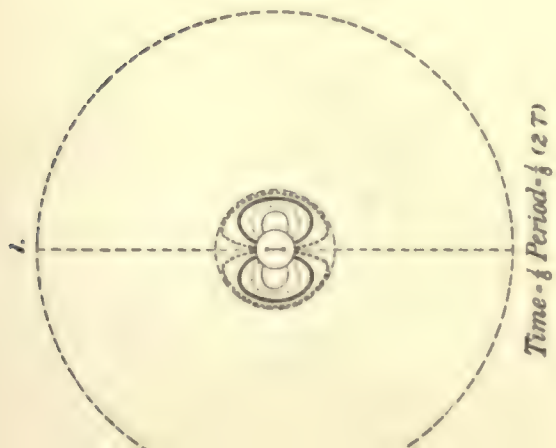
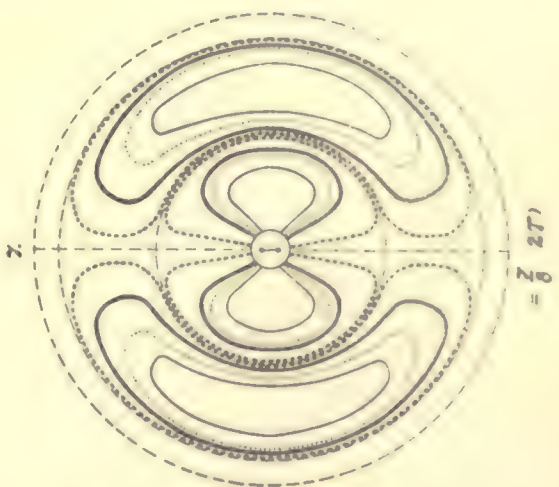
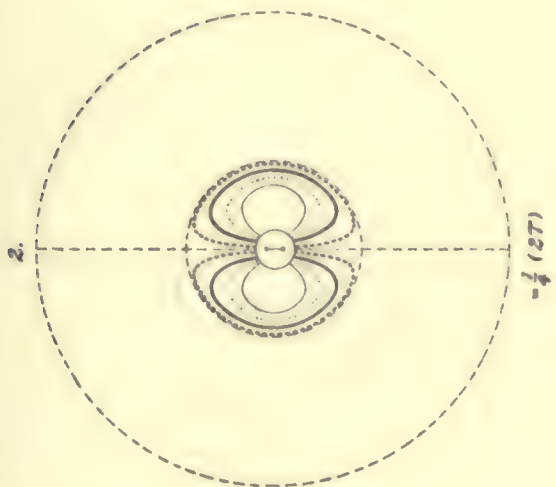
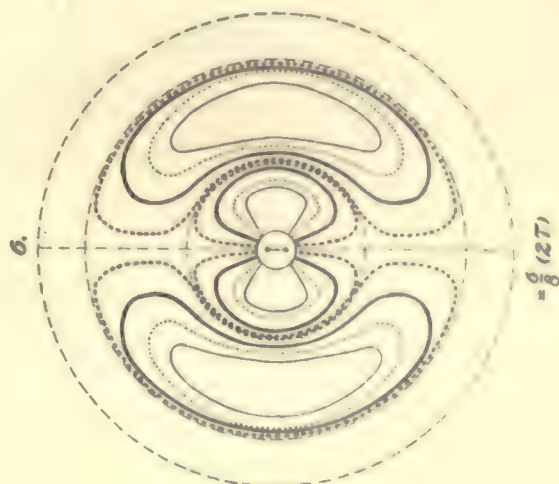
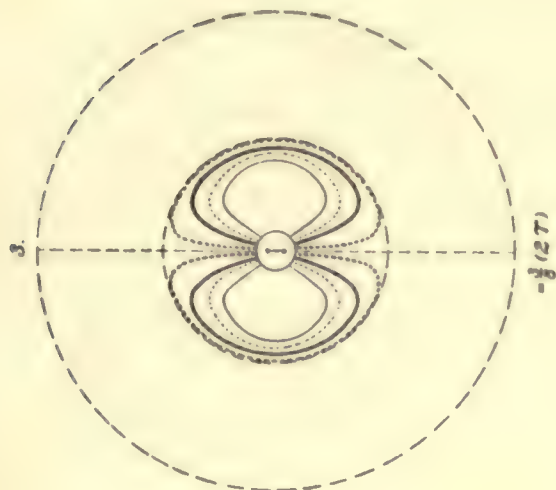
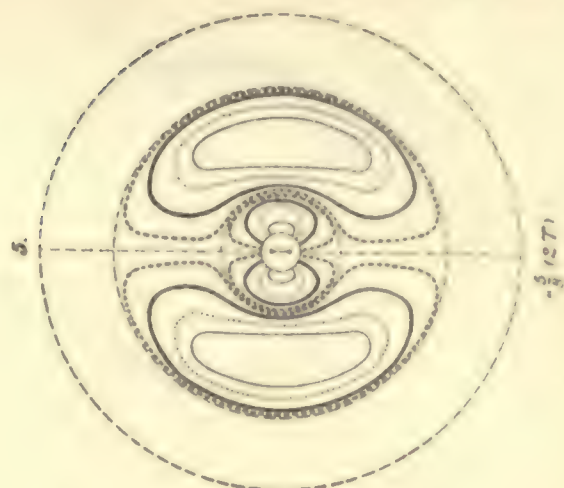
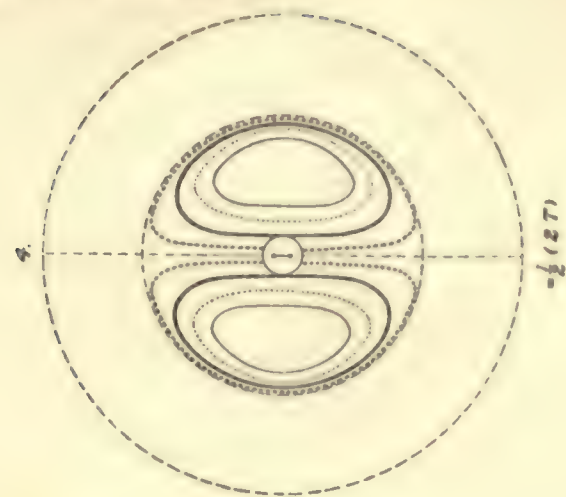
The waves of magnetic force and of component axial electric force move outwards each with the same velocity at all points, and this velocity is equal for all points at the same distance from the oscillator. The intensity of the first force for points on the same sphere varies as the cosine of the latitude, but that of the second force is constant. The wave of component transverse electric force moves outwards with equal velocity for all points at the same distance from the oscillator, and its amplitude varies as the cosine of the latitude. Its velocity after it has reached a certain distance from the origin, is always greater than that of the waves of component axial electric force, and of magnetic force, and its excess over the velocity of light tends to become three times the excess of the velocity of the wave of magnetic force over the velocity of light.

(iii.) The velocities of these waves undergo remarkable changes in the neighbourhood of the oscillator, but still at distances such as HERTZ experimented at, and which seem indeed to some extent within the field of possible physical investigation.

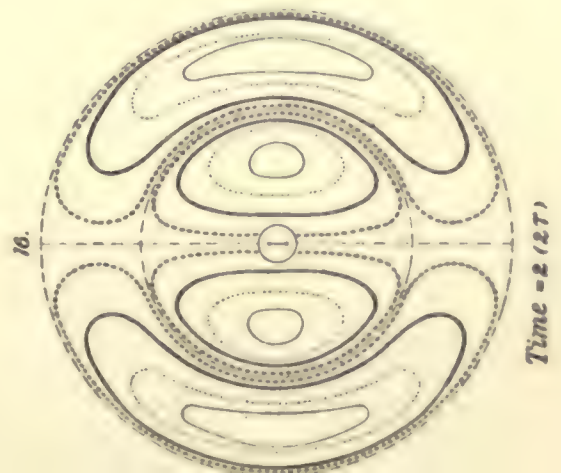
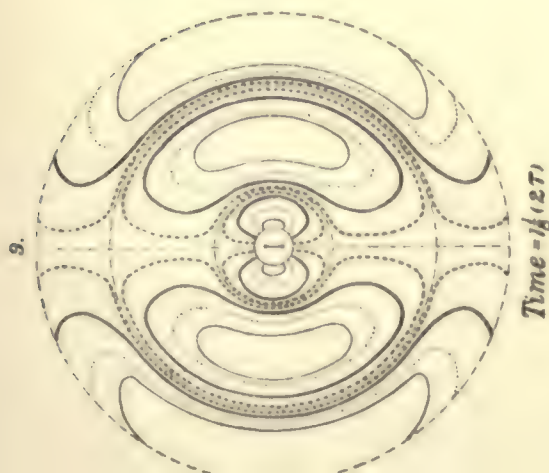
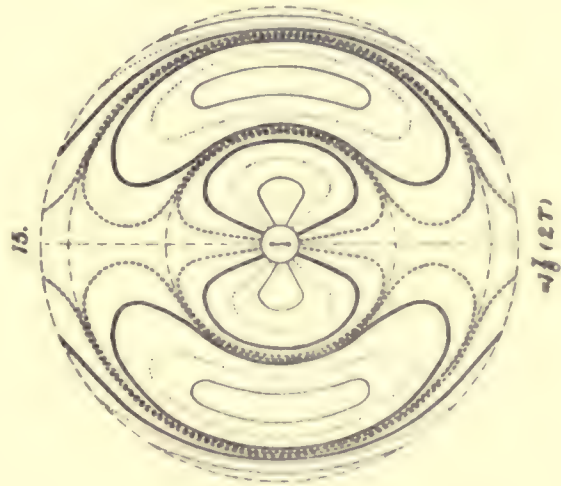
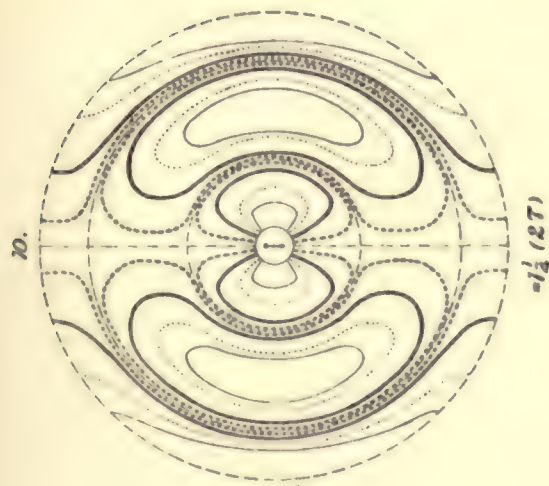
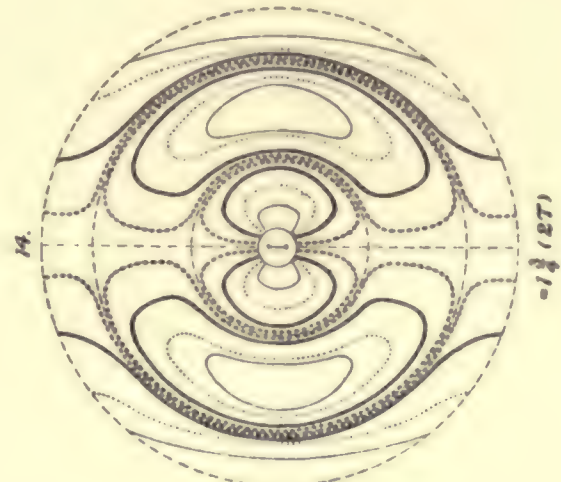
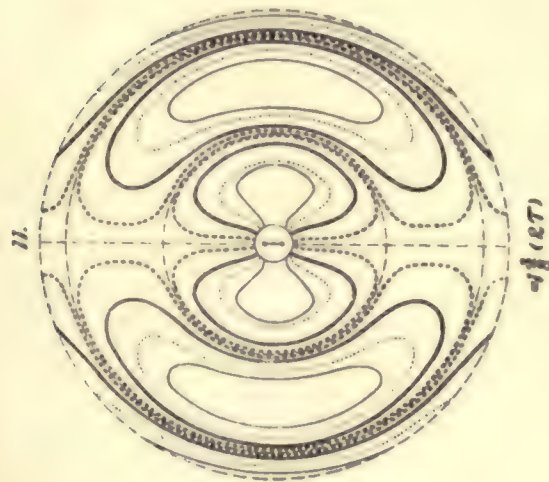
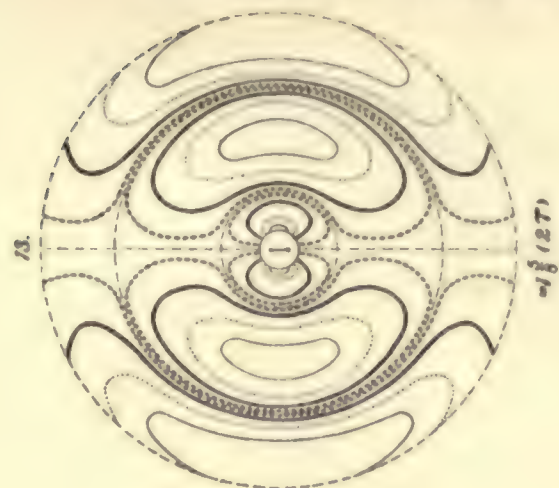
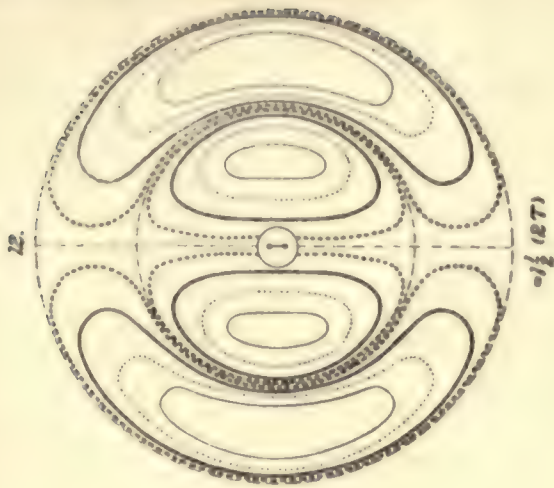
(iv.) The point of zero phase for both transverse and axial component electric waves does not coincide with the centre of the oscillator, so that these waves appear to start from a sphere of small but finite radius round the oscillator. A fourth wave dealt with by HERTZ, the wave of magnetic induction, does not, as he supposes, start from the centre of the oscillator with zero phase, but in the case of a damped wave train with a small but finite phase.

(v.) Our analysis of these waves and of their singular points in the neighbourhood of the oscillator appears to add something to HERTZ's discussion; it is possible that it may throw light on the difficulties which arise in connecting with some of his interference experiments. It would seem to us that all interference experiments ought to be made at distances greater than 6 to 7 ($\lambda/2\pi$) from the centre of the oscillator, roughly about a wave-length from the oscillator, whereas HERTZ rather terminated than started his experiments at this distance. At such distances the phase curves are approximately parallel to their asymptotes.

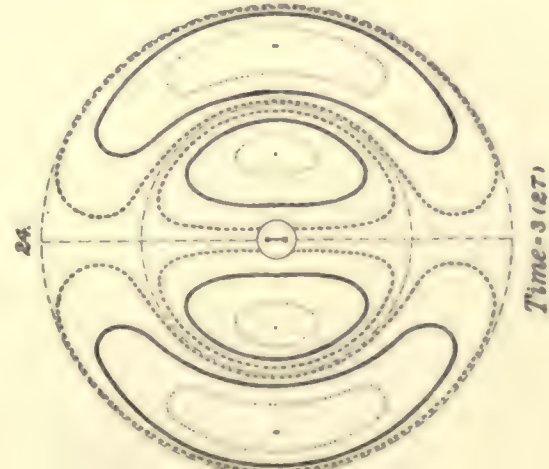
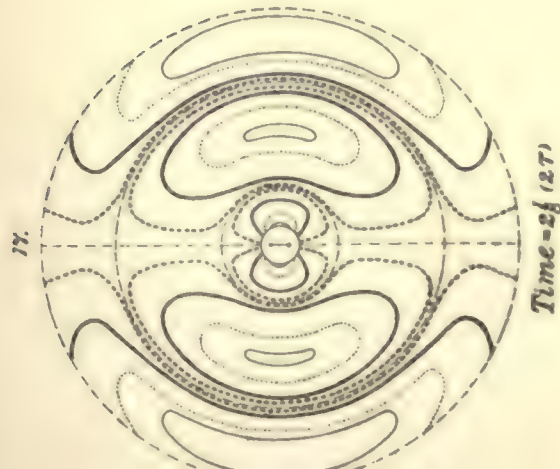
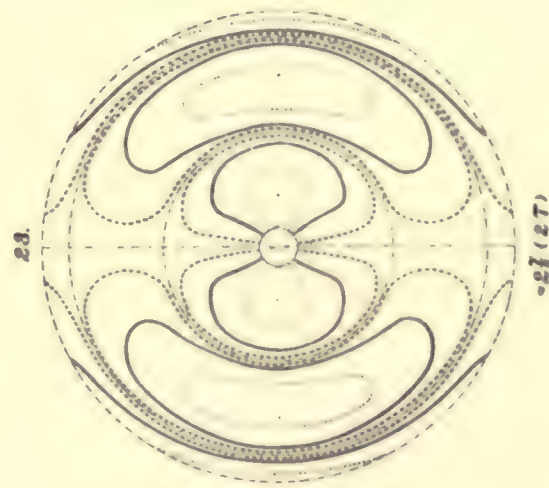
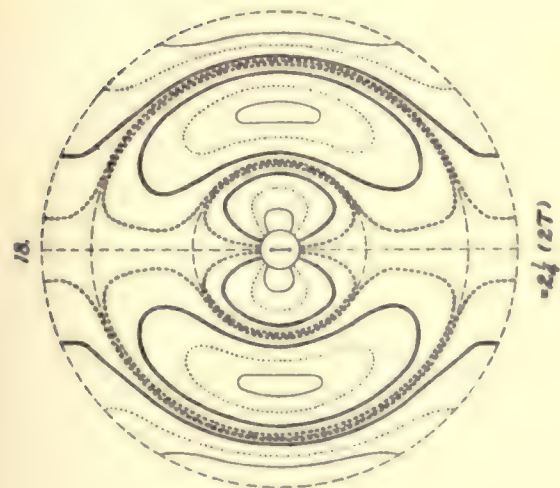
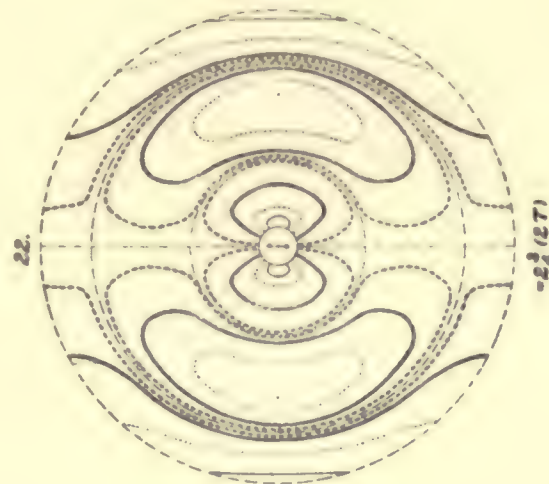
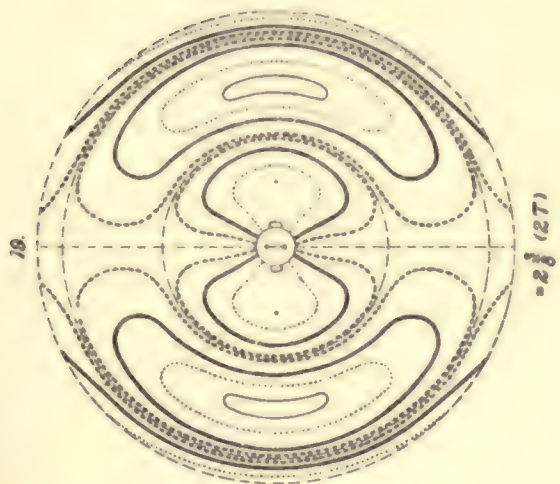
Finally, we are not unaware of the physical difficulties attending experiments, at such distances, and wish in conclusion to again emphasise the fact that our analysis only applies to a *theoretical* type of oscillator. It is, however, the type for which HERTZ himself endeavoured to provide a mathematical investigation.



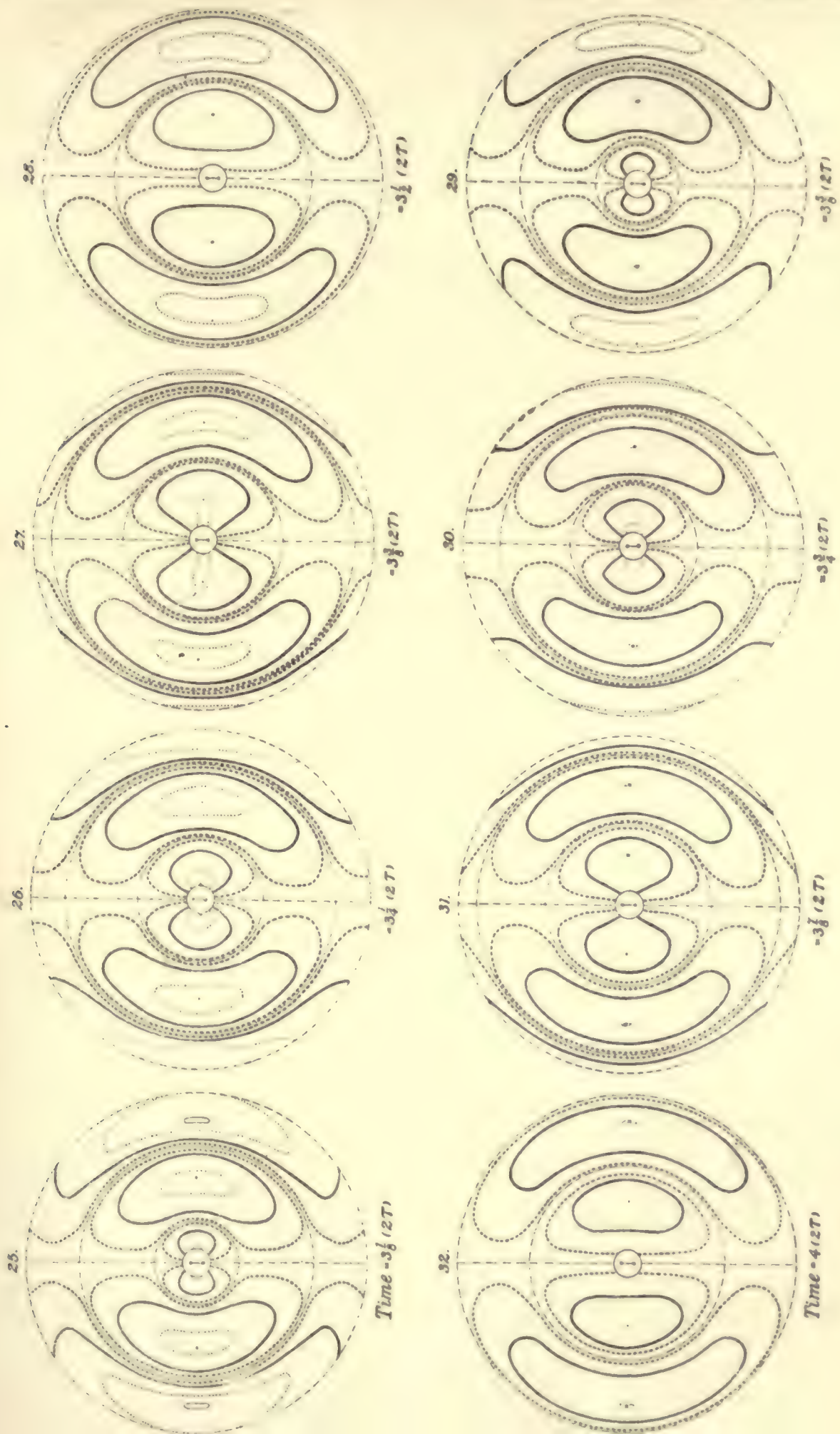


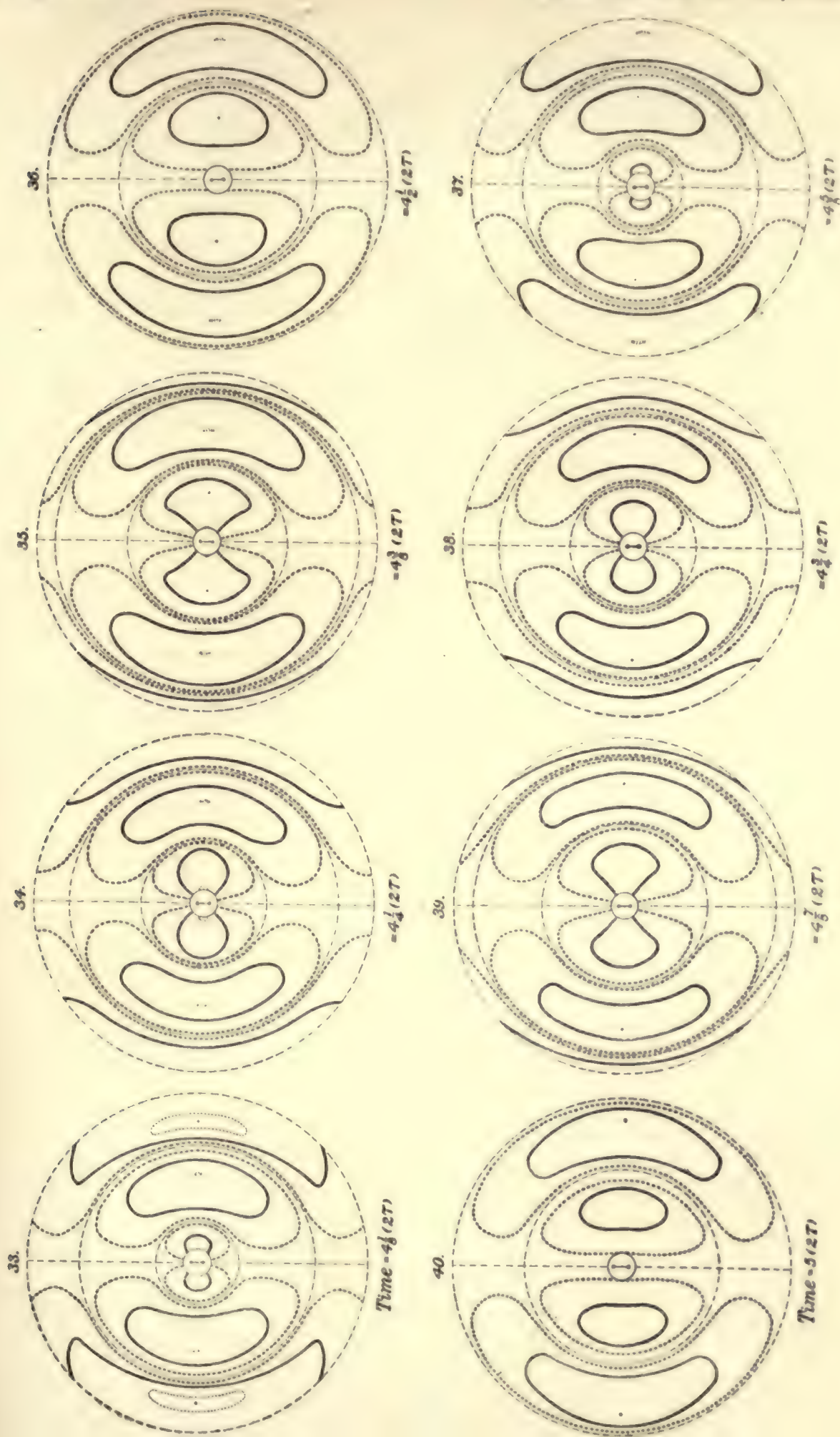




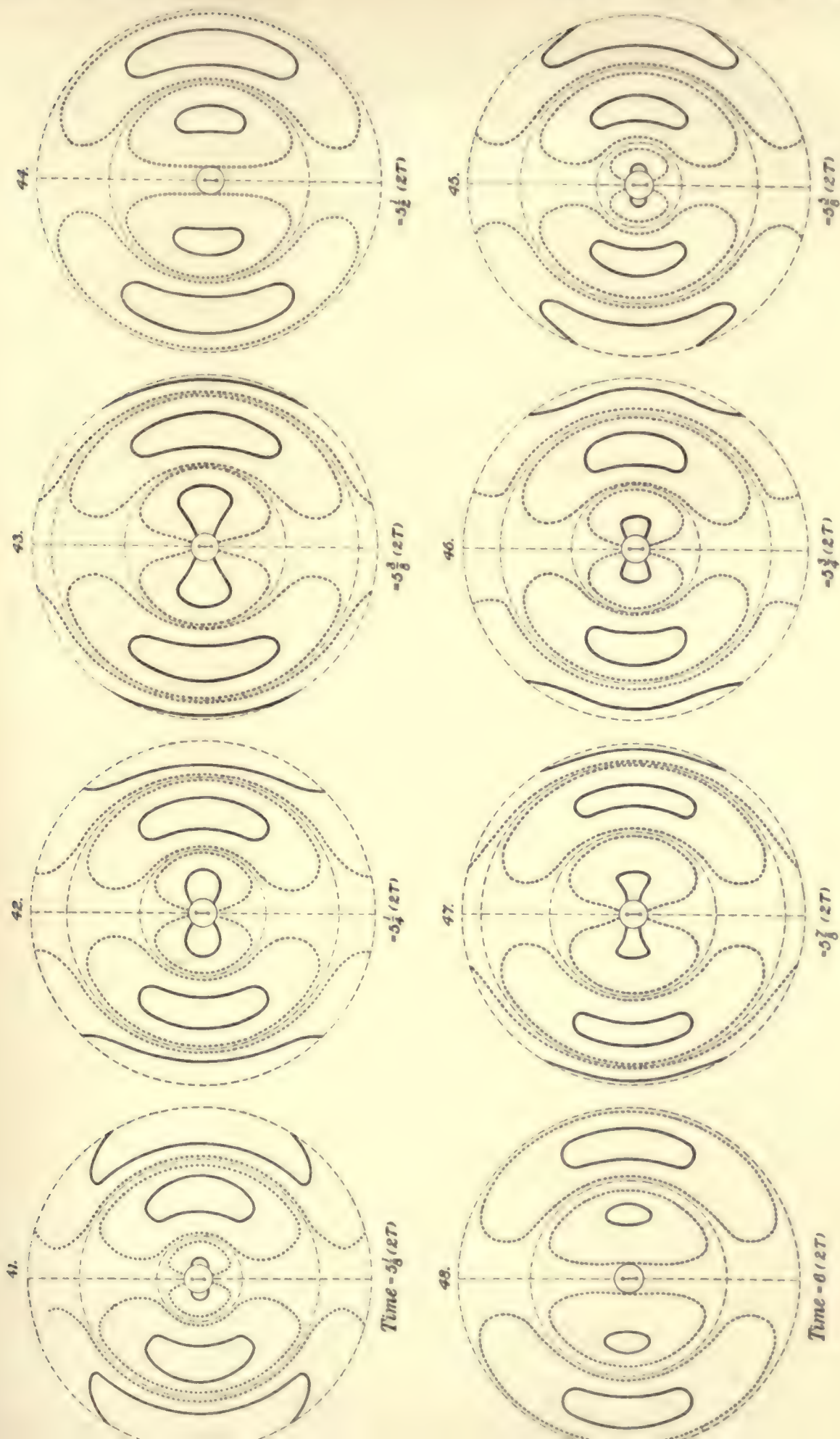


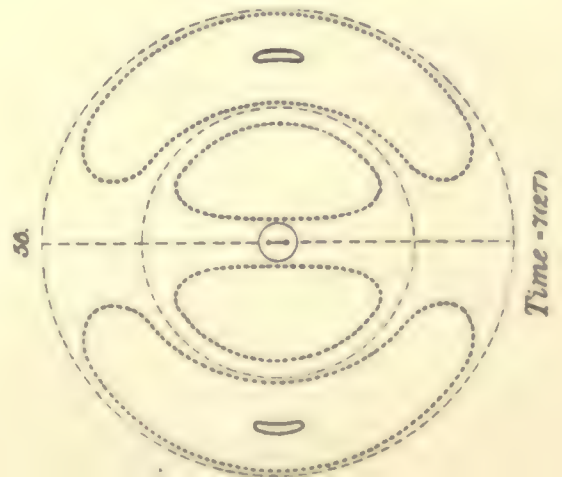
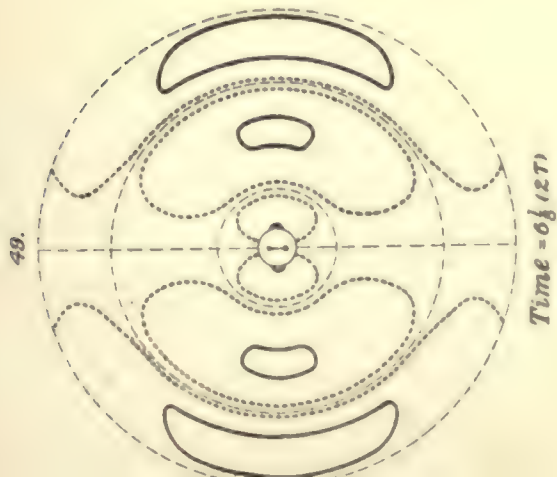
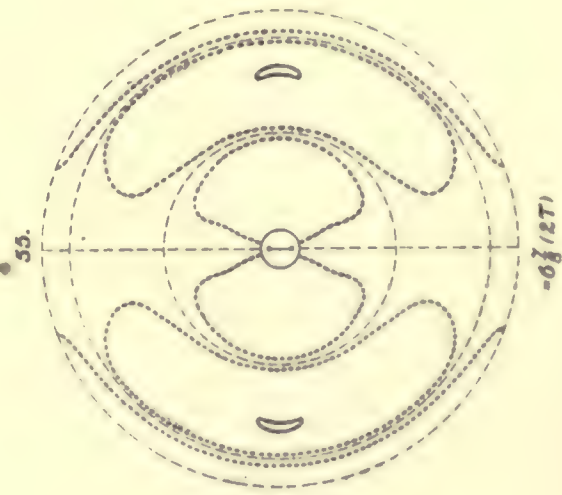
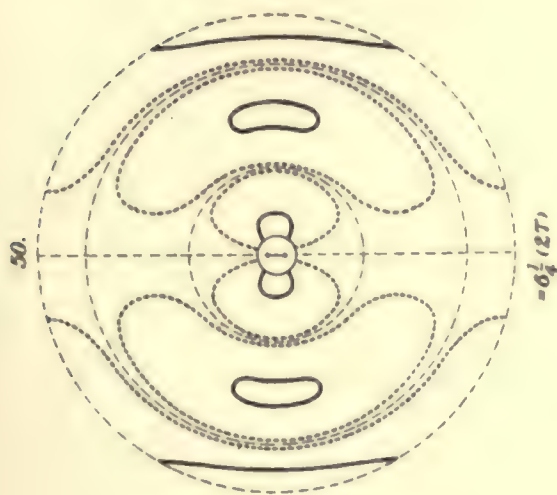
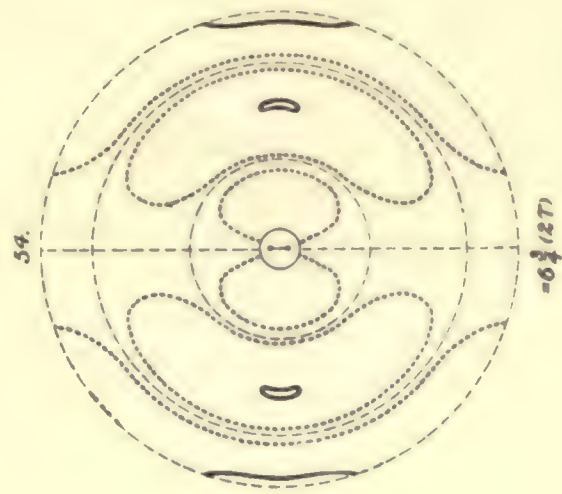
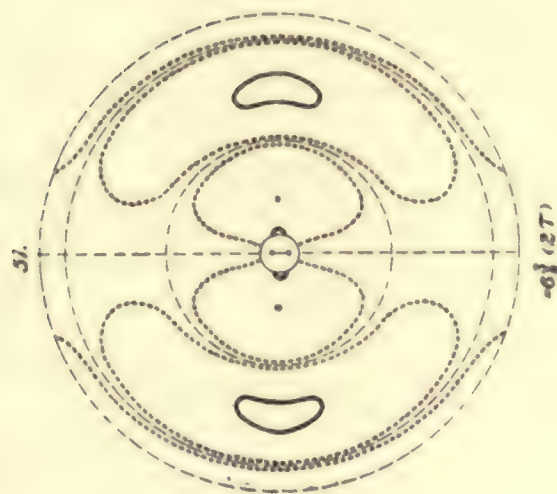
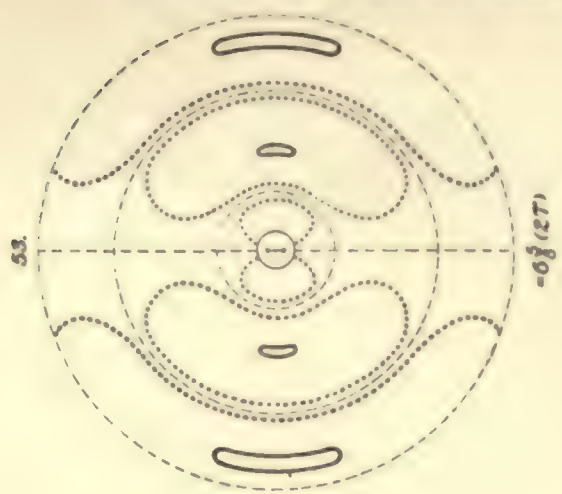
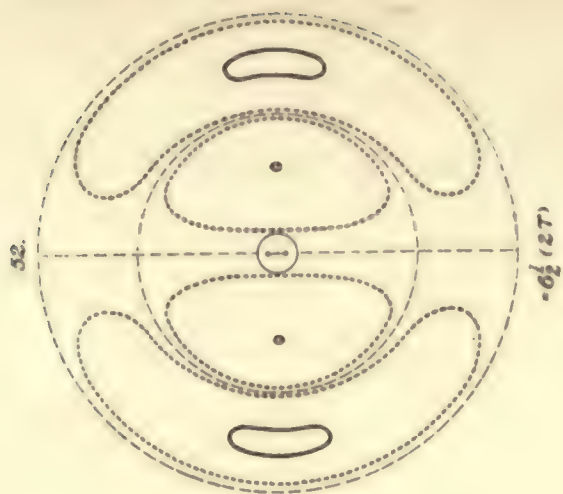












VI. *On the Constitution of the Electric Spark.**By* ARTHUR SCHUSTER, *F.R.S.*, and GUSTAV HEMSALECH.

Received February 2,—Read February 2, 1899.

[PLATES 8-12.]

1. *Object of Research and Description of Apparatus.*

WHEN an electric spark passes between metallic electrodes, the spectrum of the metal appears not only in immediate contact with the electrodes, but stretches often across from pole to pole. It follows that, during the short time of the duration of the spark, the metal vapours must be able to diffuse through measurable distances.

The following investigation was undertaken primarily to measure this velocity of diffusion, with the special view of comparing different metals and different lines of the same metal.

Dr. FEDDERSEN* published in the year 1862 an interesting research in which photographs of sparks were taken after reflection from a rotating mirror. He was able to draw some important conclusions from his experiments, but it was necessary for the more detailed examination we had in view, to analyse the light by a spectroscope, so as to distinguish between the luminous particles of air and those of the metal poles.

Attempts to measure the required velocity, using rotating mirrors either between the spark and the slit of a spectroscope or between the prism and telescope, were made by one of us at various times during the last fifteen years. They failed because the method requires that the spark should pass when the mirror is in the same position, and no satisfactory device could be found to secure this object, without at the same time complicating the spark circuit, which it was necessary to confine as much as possible to the electrostatic capacity and spark gap.

Instead of using a rotating mirror, it is possible to secure the same object by taking photographs in a rapidly moving film. An arrangement of this kind was employed by Professor H. DIXON in his experiments on explosions, and proved at once successful.

The principle of the method is extremely simple, and may be employed in all cases

* 'Pogg. Ann.,' vol. 116, p. 132 (1862).

where each spark is of sufficient intensity to give a good spectrum. A sensitive film is attached to a spinning wheel and the spark image formed on it. Were the spark absolutely instantaneous, the images taken on the rotating wheel would be identical with that taken on it when stationary, but on trial this is found not to be the case. The metal lines are found to be inclined and curved, and their inclination serves to measure the rate of diffusion of the metallic particles.

The interpretation of the photographs presents no difficulties if the velocity of the film is everywhere at right angles to the direction of the slit. Such is the case in Professor DIXON's experiment, and our first wheel was nearly a copy of that used by him. Fig. 1 shows the section of this wheel; the axle bears at A and B against strong screws fixed in a cast-iron support, not shown in the figure. The rim of the

Fig. 1.

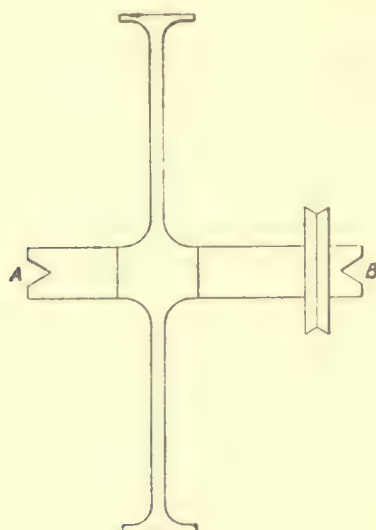
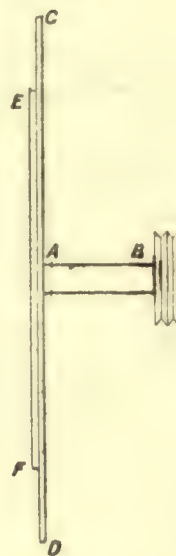


Fig. 2.



wheel had a width of 4 centims., its diameter was 30 centims. The photographic film was wound round the rim, and, although good results were obtained with this wheel, some difficulty arose from the tendency of the film to fly off. Several methods of fastening it to the rim were tried, but the only one which proved satisfactory was to tie it down by two strong steel wires, stretched tightly round the whole circumference. Velocities of about 80 revolutions a second could be obtained, but at the high speeds the film lifted up along the central line, just where the spark images fell.

A new apparatus was now constructed for us by the Cambridge Scientific Instrument Company, and is illustrated by figs. 3, 4, 5 (Plate 8), while fig. 2 shows a section of the moving parts. The film is placed flat against a steel disc, CD, and is kept in place by a second steel disc, EF, which presses against it, being secured by small screws,

shown in fig. 4. The ball-bearing, AB, consists of the hub and axle of a bicycle pedal, the hub being supported by two sets of three strong twisted cords, stretched and fixed as shown in fig. 3, which gives a back view of the apparatus. The same figure also shows a narrow vertical tube for oiling the bearing. The moving parts are surrounded by a circular cast-iron box, which can be covered both in front and at the back. The light forming the image of the spectrum passes through a rectangular aperture cut into the front cover. Fig. 4 (Plate 8) gives a front view with the smaller disc detached and placed in front of the cover. Fig. 5 (Plate 8) shows the whole apparatus ready for experiment. The driving power was a half h.-p. electric motor capable of revolving 33 times a second, and carrying a disc with three grooves. The disc was provided with two pulleys of equal size, so that at high speeds it might be driven from two motors at opposite sides, thus avoiding the side pull. The motor and spinning wheel were tightly clamped to the table of a lathe, in such a way that the apparatus could be dismantled and put together again, with all parts occupying the same position. This was of importance, the method of focussing adopted rendering the removal of the disc necessary during part of the operation. The diameters of the two steel discs were 33 and 22.2 centims., the photographs being taken in the annular space of 10.8 centims., left free when the smaller disc was placed on the larger one.

In all the experiments the driving cord was passed round the second pulley of the motor, which had a diameter of 21.7 centims., while the groove of the pulley on the spinning-wheel was cut to 2 inches, or 5.1 centims. The speed of the motor was measured by an indicator of ELLIOTT BROTHERS, which was tested and found correct. The ratio of the angular velocities of motor and disc might be obtained approximately by calculation from the diameter of the pulleys, allowance being made for the thickness of the cord, or we might turn the motor slowly by hand, counting the number of turns of the disc at the same time. For our purpose this would have been sufficient, as the other uncertainties of the experiments do not at present allow a very great accuracy, but in order to avoid any doubt, and on account of the interest which attaches to the amount of slipping which takes place at high speeds, an independent stroboscopic method was employed to determine the ratio of the angular velocities. We were surprised to find no measurable slip, except at the highest speeds, such as were never used by us in our experiments.

In our experiments the disc revolved generally about 120 times a second, giving a linear velocity of between 90 and 100 metres per second for that part of the film on which the photograph was taken. When the cord was passed over the largest pulley of the motor we could spin the disc over 160 times a second; this was tried and the speeds were tested, but no photographs were taken, as the smaller velocities gave us sufficiently good results.

Our first successful experiments were made with a single-plate Voss machine, the discharge being taken from four Leyden jars in the circuit, but the beauty

of the photographs was considerably increased when a much more powerful battery was introduced, and charged from an induction machine constructed for us by Mr. H. C. WIMSHURST. This machine has 12 plates, of 62 centims. diameter, and gives, without jars, sparks which are 13 inches long. In the majority of our experiments six large jars of flint glass were used, each jar having a coating of tinfoil, of about 2000 sq. centims. surface. The capacity of each jar was measured separately for us by Mr. J. R. BEATTIE, and found to vary from '0049 to '0060 microfarad, the capacity of the complete battery being '033 microfarad. The jars, which had not been used for years, were found to be in bad condition. They were carefully cleaned, by soaking first in caustic soda and then in nitric acid. After coating with tinfoil to within 10 centims. from the top, the uncovered parts were heated in front of a fire to over 60° C., so as to secure complete dryness, and then, whilst hot, varnished. After this treatment the jars gave no trouble.

Great care is necessary in handling a battery of this capacity, especially as the experiments are conducted in the dark.

Fig. 7.

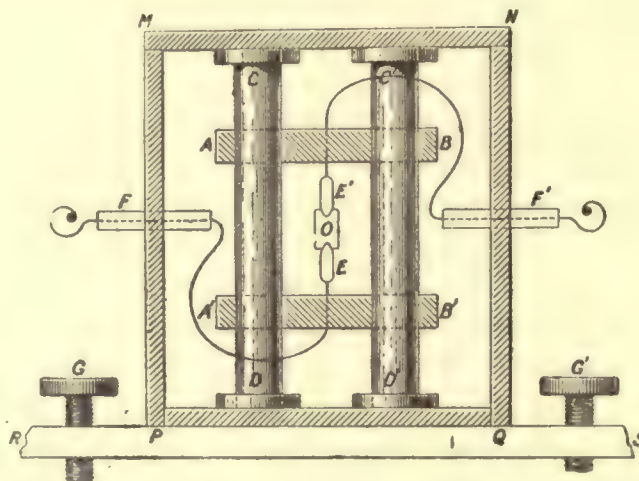


Fig. 6.



The whole battery was placed together on an insulated table, and Mr. WIMSHURST's recommendation to keep one hand always in the pocket while handling the jars also proved useful.

The metal electrodes were fitted inside a box having an opening towards the collimator of the spectroscope. Perhaps the greatest source of trouble at first consisted in the uncertainty of the position of the points on the electrodes, from which the sparks set out. Successive sparks did not always leave the poles at the same points, so that the spark images did not always fall centrally on the slit. This was remedied to a great extent by giving careful attention to the shape of the electrodes and to their polish. The form adopted after a few trials was conical, and is shown in fig. 6. The metal having first been turned in the lathe to the required shape, was

polished by means of emery paper, and finally by wash-leather. Good polish was found necessary to prevent sharp projections, which, though they may be small, cause premature discharges before the jars are sufficiently charged.

A section of the electrode box is shown in fig. 7. It is made of wood and is fixed to a board, RS, capable of being levelled so as to make the spark path as nearly as possible parallel with the slit. The electrodes are fixed to two wooden plates, AB and A'B', which are attached to flint-glass tubing, CD and C'D', the glass being carefully varnished. The electrodes, E, E', are connected to the Leyden jars by means of gutta percha-covered wire (No. 18) which passed, as shown in the figure, through apertures in the plates, AB, A'B', and finally through glass tubes, F and F'. The leads from the jars were hooked to loops formed by the wires attached to the poles, the sharp ends of all wires being protected by means of small spheres of sealing-wax. We used in the experiments a standard distance of 1 centim. between the electrodes. The electrodes having been fixed to the plates, their distance was adjusted and the plates secured to the glass rods by means of sealing-wax.

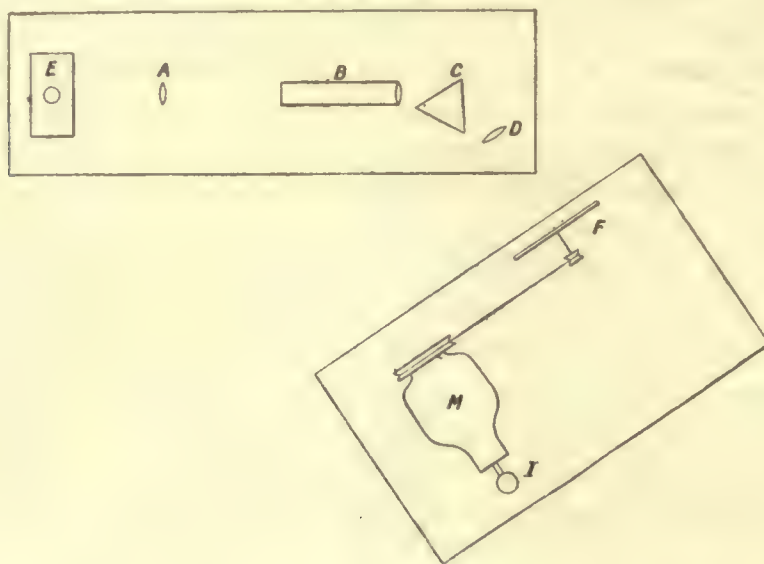
A few words should be said about the optical arrangements. It was for our purpose most important to have a good image of the spark in coincidence with the slit. As we confined our investigation principally to that part of the spectrum which, with glass prisms and lenses, is photographically most intense, the lenses were specially made for us by Messrs. ZEISS at Jena, the chromatic and spherical aberrations being corrected for the region F to H of the solar spectrum. When it is required to form a spark image on the slit, sufficient attention is not always given to the fact that lenses are generally constructed to be used with a parallel beam of light. The aberrations introduced when objects at small distances are to be focussed, are sometimes considerable, and had to be avoided in our experiments. We asked Messrs. ZEISS therefore to make a lens of 4 centims. aperture and 25 centims. focus, which when placed at a distance equal to twice its focal length from the spark, should give an image equal in size to the object within the required limits of the spectrum, free from chromatic and spherical aberrations. The lens sent to us answered all our requirements perfectly. Both collimator and camera lenses had apertures of 4 centims., and focal lengths of 46.3 and 39.9 centims. respectively. The prism used was made of old flint glass by STEINHEIL, having a refracting angle of $59^{\circ} 28'$ and a refractive index of 1.6227 for sodium light. The extent of the spectrum between F and H on the revolving disc was about 1.5 centim.

The general arrangement of the apparatus is shown in a diagrammatic form in fig. 8. E represents the electrode box, A the lens forming the image of the spark on the slit of the collimator B, through which the light passes before it is dispersed by the prism C and focussed by the camera lens D. The parts A, B, C, D were mounted on a slate slab secured to the wall by means of strong brackets. The lathe support which carried the motor M and spinning disc F, was placed so that the image of the

spectrum should fall near the top of the disc vertically above the axle. I represents the indicator which shows the speed of the motor.

The adjustments which it is necessary to carry out with accuracy consist in the focussing of the spark image on the slit, the proper centering of the apparatus, and the focussing of the camera lens. In addition to this, it was found convenient to place the lens A as nearly as possible half-way between the spark and slit, so that the spark image on the slit should be of the same magnitude as the spark. This rendered the interpretation of the photographs more easy, as the linear dimensions measured in the direction of the spark discharge were reduced in that case by the optical arrangement in the fixed ratio of the focal lengths of the camera and collimator lenses, viz., '86. One millimetre in length of the slit images therefore always corresponded to 1.16 millim. in length of the spark path.

Fig. 8.



The adjustment of collimator and lens A is most easily carried out if the prism C and lens D are removed, so that a clear view can be obtained through the collimator towards the spark box. The collimator was adjusted in the usual way for infinite rays. As it was separately supported on a tripod stand, it could be accurately levelled, and the centre of the slit placed, by means of a cathetometer, accurately at the same height as the centre of the spark gap. The focal length of the lens A being known, the distance between the spark and slit was adjusted by measurement to be equal to a little more than four times that focal length, and the lens A was placed at the right height, and exactly half-way between the slit and spark gap. Sparks from an induction coil were now allowed to pass between the electrodes, the slit being opened wide, and a telescope adjusted for infinite rays placed in front of the collimator, so that the observer obtained a clear view of the slit. If the adjustment is good, the

electrodes illuminated by the spark are in perfect focus. By a few successive trials, in which the electrode box and lens A alone were moved, and in such a way that the latter was shifted through half the distance of the former, this could always be secured, and at the same time the lens kept half-way between spark and slit.

The lens A had now to be temporarily removed, to make sure that the axis of the collimator pointed to the centre of the spark gap. For this purpose the collimator lens was covered by a piece of cardboard with a central slit about 2 millims. wide, and the electrode box shifted sideways until the maximum amount of light passed through this slit. Replacing the lens A into its previous position, it is easy to ascertain that the adjustment of distances has not been disturbed. The adjustment being complete, the correct position of collimator was permanently secured by pouring melted paraffin wax round the tripod screws which carry it. The lens A was fixed in the same way, but a lateral motion of the electrode box must be allowed, so as to correct the small displacements which necessarily occur when one set of electrodes is replaced by another.

The prism is placed in the usual way in its proper position in front of the collimator; we worked in a position of minimum deviation for a wave-length of about $4.3 \cdot 10^{-6}$.

The only remaining adjustments are those of the camera lens and disc. The lens D was fixed to a brass tube which could be made to slide in a collar by means of a screw. The lens was placed so that it was completely illuminated by light passing through the collimator and prism; this is easily tested by an eye placed at the focus of the lens.

When the position of the disc had been accurately fixed, so that the spectrum was formed at the proper place, a film, which had to be sacrificed for the purpose, was placed on the disc just as during an experiment. A pointed rod was now brought into contact with the film and against some prominent spectrum lines like the blue triplet of zinc. The rod was fixed in this position, slightly touching the film, so that the disc could be rotated without appreciable friction. The disc was now removed for the final adjustment of focus, an eye-piece being put in position, so that the pointed end of the rod was in its focal plane. If the lines of the spectrum were not in focus, the lens D were moved until that was the case. The wheel being then replaced into contact with the rod, a perfect focus was secured.

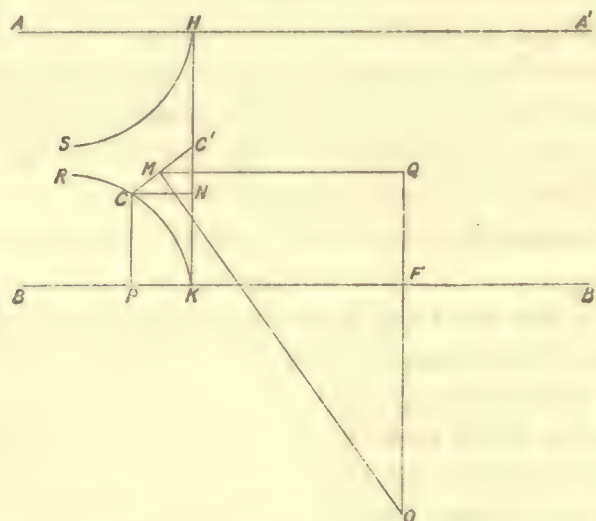
The different parts of the spectrum were not situated at equal distances from the axis. A slight correction which may in consequence be necessary in the reduction of the observations, requires the knowledge of the point of the spectrum which lies at the minimum distance from the axis, *i.e.*, if the spectrum is horizontal, we want to know the wave-length lying vertically above the axis. This may readily be ascertained by suspending a plumb-line close to the disc passing in front of its centre. The shadow of the string will then show on any photograph of the spectrum which is taken.

2. *Interpretation of Photographs.*

With the wheel which was first used, the film was placed round the rim (fig. 1

and the velocity of the film being everywhere at right angles to the image of the slit, the interpretation of the photographs was obvious. But with the film on the face of the disc, as in our final experiments, the linear velocity is not the same for different portions of the slit image, or different parts of the spectrum, nor is it everywhere perpendicular to the slit image. The following investigation shows how the velocity of the particles may be deduced from the measurement of the photographs.

Fig. 9.



Let AA' (fig. 9) represent the upper, and BB' the lower, edge of the spectrum, as it would be formed on a stationary film. KH represents the monochromatic image of the slit at the instant of the beginning of the discharge, and KR , HS the curved edges of a spectroscopic line as they appear on a photograph taken with a moving slit. The displacements are most easily determined by measuring the coordinates $PC = y$ and $NC = x$ parallel and at right angles to HK . If O be the centre of the disc, a point, C' , of the slit image will describe a circular arc, $C'C$, on the moving film, and the time taken by the moving particle to go from K to C' is the same as that which the point C of the disc takes to describe the arc CC' , which may for our purpose be taken as equal to the length of the chord. From the middle point of CC' draw the lines MQ perpendicular to HK , and QO parallel to HK . Then

$$C'N : NC = MQ : OQ,$$

or if $KC' = z$, $OF = a$, $FK = b$, and if the squares of y and z and their products are neglected, compared to a^2 ,

$$z - y = bx/a.$$

For the line HS we should similarly find $z - y = -bx/a$. Also from the figure

$$CC' : CN = OM : OQ,$$

or writing s for CC' and r for OM ,

$$s : x = r : a + \frac{1}{2} (y + z).$$

Again neglecting the square of small quantities,

$$s : x = r : a + y.$$

It is convenient to introduce in place of a the distance (c) between O and the *centre* of the spectrum, so that $a = c - h$, where h represents half the width of the spectrum. To the required degree of accuracy it is then found that

$$\frac{s}{x} = \frac{r}{c} \left(1 \pm \frac{h - y}{c} \right),$$

where the minus sign refers to measurements taken along HS .

The time (t) taken for the description of the arc CC' is $s/r\omega$, ω denoting the angular velocity of the disc, and if v be the linear velocity at the centre of the spectrum

$$t = \frac{sc}{rv} = \frac{x}{v} \left(1 \pm \frac{h - y}{c} \right).$$

As y and x are obtained by measurement of photographs, and h and c have been practically constant in the experiments (though also measured in each case), the above equations allow us to calculate

$$z = y \pm \frac{bx}{c}, \quad t = \frac{x}{v} \left(1 \pm \frac{h - y}{c} \right).$$

If x_1, y_1 , and x_2, y_2 are the measured coordinates of two points lying near each other on the curved images of the spectroscopic lines, the velocity of the luminous particles at the corresponding point of the spark will be $K \frac{z_2 - z_1}{t_2 - t_1}$, where K is the ratio of the length of the spark gap to that of its image on the film, which in our case was simply the ratio of the focal lengths of the camera and collimator lenses, i.e., 1.16. If both poles are made of the same material, so that both the lines which appear at the top and bottom of spectrum can be measured and the mean taken, the correction disappears, and the velocity of the particles is given directly by $Kv \frac{y_2 - y_1}{x_2 - x_1}$. Even when a line can only be measured on one side, this may approximately be taken to be the velocity, for in our experiments c was equal to 14, the distance b was seldom greater than 1 and never greater than 2, while the ratio x/y was always less than $\frac{1}{3}$, so that z and y only differed at the maximum by 5 per cent. from each other. The uncertainty of our experiments, for reasons which will be given, was greater than that amount. Similarly may the quantity $\frac{h - y}{c}$ be neglected for the present.

3. *Method of Conducting Experiments and Measurement of Photographs.*

The method of conducting an experiment is obvious from the preceding descriptions. The apparatus being in adjustment, a photograph was taken of the spark spectrum, on the stationary disc. This is for the sake of reference, chiefly for the purpose of identifying the lines. The disc was then set spinning and when the desired speed was attained and found to be uniform the Wimshurst machine was set going by hand until about six sparks had passed. We thus obtained a number of images on each film, some of which sometimes were found accidentally to overlap. The images are not found to be equal in clearness, the spark not always passing parallel to the slit; the two best were selected for measurement. For this purpose the film, after the images had been developed and fixed, was cut up, each image being carefully marked for future reference.

The measurements were made by means of a "comparator," a very beautiful instrument, made by ZEISS, of Jena. The instrument consists essentially of two microscopes at a fixed distance from each other. A sliding table underneath serves to carry the photograph to be measured under one microscope and a scale under the other. A photograph having been fixed to the table by means of soft wax, a fine adjustment screw allows a certain relative displacement between it and the scale, so that when any desired line is in the centre of the field of view of one microscope the scale may be read with the other, and adjusted to give any desired reading. This adjustment is of great convenience in the comparison of different spectra with each other, as some air line, common to all, may always be placed so that the reading is in every case the same. The scale is divided into $\frac{1}{5}$ millims., and a micrometer eye-piece allows readings to $\frac{1}{1000}$ millim.

Speaking for convenience sake of the slit images as "vertical," the photograph must be placed so that when the sliding table is moved the trace of the centre of the field of view on the photograph is horizontal, and the measurements consist in measuring the horizontal displacements of each spectrum line at different distances from the edges of the spectrum.

Our first method of conducting the measurement was to take contact prints on glass of the selected images. On these copies horizontal equidistant lines were ruled by a fine needle point fixed to a dividing engine. The displacements could then be measured along each of these lines. The disadvantage of this method consists in the labour of taking copies and ruling lines, and also in the loss of definition, which, however small, was always noticeable in the contact print. At a later stage, therefore, the method of measurement was changed to the following:—A brass frame was made in which the film could be clamped so that it lay perfectly flat under the microscope. Underneath the photograph was placed a transparent scale, made of a portion of a film from which the sensitive layer had been removed, and on which horizontal lines at a distance of about .55 millim. had been ruled. These lines could

be seen in the instrument traversing the spectrum horizontally. They served as reference lines along which the displacements could be measured.

Accurate measurements of wave-lengths were not necessary for our purpose as long as we could identify the different lines. As the prism was not disturbed during the principal series of our experiments, the air lines were found to be sensibly at the same distance from each other in all our photographs. Making use, therefore, of a few of these air lines, which are sharp, and of the lines of zinc and cadmium, which are easily identified, a curve may be drawn from which the wave-lengths corresponding to any reading of the comparator may be determined in the usual way with quite sufficient accuracy.

4. *Preliminary Experiments.*

Before entering into the main subject of our research, we desired to become familiar with the appearance of the spark itself, and with such other phenomena connected with it as could be elucidated by photographs of the spark itself. We describe the results obtained, selecting out of a number of plates those which seem to present distinctive features of interest.

Fig. 11, Plate 9, November 10, 1897.—Image of spark taken between zinc and brass electrodes; 5 Leyden jars were used, their total capacity was not measured, but the jars were smaller than that of the battery of six used in the later experiments, and the total capacity was estimated to be about half, *i.e.*, about $\cdot 015$ microfarad. The chief feature of this photograph is a slightly curved very luminous column, containing, as was subsequently ascertained, the first discharge breaking through the air. This is surrounded by a cloudy appearance, which is due to the metallic vapours generated by the first discharge.

Our later experiments, to be described further on (p. 211), point to the conclusion that the oscillations following the first discharge pass through this cloud of metallic vapour. Some sharp linear luminous filaments may be seen in the original on one side of the main discharge. These set out from small projections on the electrodes and precede the main discharge, as may be ascertained by carefully watching the image on the focussing plate of the camera. The preliminary discharges may be avoided by giving careful attention to the polish of the electrodes.

Fig. 12, November 10, 1897.—A photograph of the spectrum of the preceding discharge, taken with 15 sparks. The image of the central column was thrown on the slit. The spectrum is that of zinc and air, with one or two lines of copper, and apparently the calcium lines H and K. A trace on the calcium line at 4227 also shows on the original.

Fig. 13, Plate 9, November 10, 1897.—The same as fig. 12, except that the cloudy portion of the discharge was focussed on the slit, which had to be widened a little in this case. Thirty sparks had to be taken to secure an impression which could be compared in intensity with the previous one. The absence of air lines, verified also by

eye observations, proves that the cloudy luminosity is due to metallic vapours. The presence of metallic lines in fig. 2 does not prove the presence of metallic molecules in the main discharge, as it is impossible to obtain an image of the latter free from that of the luminous cloud lying in front and behind it.

Fig. 14, Plate 9, November 12, 1897.—Spark between iron poles, showing the luminous filaments preceding the discharge.

Figs. 15 and 16, Plate 9, November 13, 1897.—Sparks taken under similar circumstances as fig. 14. In fig. 16 a current of air is blown through the spark gap. The effect of this current of air is remarkable, as the time of luminosity of the air column was found in subsequent experiments to be less than 10^{-6} second, and the actual displacement of the air during that time must have been quite inappreciable. The most probable explanation is that the spark passes through those portions of the air which have been made conducting by preliminary invisible discharges. The air put into the sensitive state by these first partial discharges has time to move over a sensible distance before the main spark passes.

It is remarkable how the metallic vapours in this photograph seem to be drawn into the glass tube.

Fig. 17, Plate 9.—Photograph of a succession of sparks taken with a small jar and large induction coil. This photograph illustrates the fact that, in the ordinary arrangement adopted to produce metallic spectra, the air discharge is predominant, while the metallic cloud is chiefly confined to the neighbourhood of the electrodes.

5. *Measurement of Molecular Velocities.*

We may now pass to the description of the results obtained when the spectrum of a single spark is taken on a moving film. A preliminary trial with various metallic electrodes had shown us that the sharpest results were obtained with zinc, and we chose, therefore, that metal for investigation under various conditions. Fig. 18 (Plate 10) gives the spectrum as we obtained it on the stationary film. The lines of zinc which appear on it are* :—

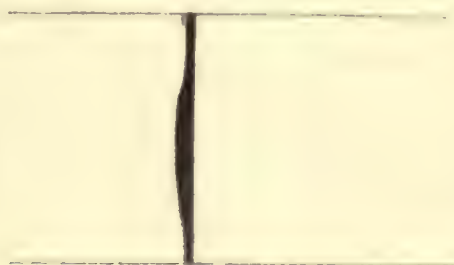
4924·8	}	α .	Zinc doublet not visible in the arc spectrum.
4912·1			
4810·7	}	β .	Zinc triplet, strong both in arc and spark.
4722·3			
4680·4	}	δ .	
4058·0	ϵ .	Not mentioned as seen in the spark by previous observers, but given by KAYSER and RUNGE as a strong line in the arc.	

* All wave-lengths are given on ROWLAND'S scale in air, and are taken from the most reliable available determinations. To identify the lines on the photographs we have attached Greek letters to the principal metallic lines shown in the figures, and these letters are also attached to the wave-lengths as given in the text.

The figure is enlarged in the ratio of about 4·2.

Fig. 19, Plate 10.—Disc spinning with linear velocity at centre of spectrum, $v = 99$ met./sec. The air lines are seen to run straight across the spectrum, but the metallic lines are curved and broadened. It follows that the metallic vapours remain luminous longer than the air lines, and that the metallic particles are projected with a

Fig. 11.



measurable speed from the electrodes. The broadening of the nitrogen doublet at 5004, marked N_1 in the photographs, only amounts to about '04 millim., which limits the luminosity as far as that line is concerned to $\frac{04}{97000} = 4 \times 10^{-7}$. The air line at 3995, and marked N_2 , is drawn out rather more, but is thinner near the poles than in the centre of the spark; its appearance, which in some of the photographs taken is even more marked than here, is illustrated in fig. 11. We must conclude that the air remains luminous in the centre of the spark rather longer than near the poles. This fact, which is very apparent for the luminosity of the metallic vapours, will be referred to again further on (p. 210).

The displacements on this photograph being the first that were actually measured, the best methods of drawing the reference lines (see p. 198) had not been adopted, and these lines were therefore at unequal intervals. In the tabular arrangement of our results we give in the first columns the coordinates of the curved lines which have actually been measured; x denoting the horizontal displacement at a distance y from the edge of the spectrum. If $y_1, y_2; x_1, x_2$ are coordinates of two points which are near together, and v is the linear velocity in metres per second, the molecular speed is $V = Kr \frac{y_2 - y_1}{x_2 - x_1}$ (p. 197), at a distance $h = K \frac{y_1 + y_2}{2}$ from the pole, where K is the factor correcting the optical reduction, which is 1·16 in all our photographs. The displacements being difficult to measure, a small error, in x_1 and x_2 near the pole, may produce very large differences in the result. For the comparison of different metals with each other we therefore calculate also the quantity $V' = Kr \frac{y}{x}$ which is the average speed between the pole and a point at a distance $h' = Ky$ from the pole;

the quantity x being larger a small error does not affect the result so largely as one in the difference $x_2 - x_1$.

TABLE I.—Zinc, $\lambda = 4810\cdot7$ (β).

Date, Feb. 15, 1898. No. XV. $v = 102$. Distance between poles: 1 centim.

x .	y .	V.	h .	V'.	h' .
millims.	millims.				
Lower pole.					
·07	·56	896	·33	896	·66
·18	1·12	631	·98	740	1·30
·38	1·66	316	1·61	530	1·93
·59	2·20	300	2·24	438	2·55
Upper pole.					
·09	·44	548	·26	548	·51
·21	·88	472	·77	506	1·02
·33	1·52	598	1·39	541	1·76
·64	2·16	241	2·13	395	2·50

$\lambda = 4924\cdot8$ (α).

x .	y .	V.	h .	V'.	h' .
millims.	millims.				
Lower pole.					
·01	·56	6632	·33	6632	·66
·23	1·12	297	·98	569	1·30
·42	1·66	347	1·61	471	1·93
·68	2·20	241	2·24	381	2·55
Upper pole.					
·10	·44	505	·26	504	·51
·24	·88	371	·77	427	1·02
·50	1·52	289	1·39	356	1·76
·75	2·16	306	2·13	340	2·50

The above experiment was only considered to be of a preliminary nature, and the photographs obtained were used chiefly to find the best method of reducing the observations, but it gives a good idea of the general nature of the results. It is seen that the velocity near the pole is a very uncertain quantity, owing to the sources of error which will be discussed (p. 210), but the velocity gradually diminishes, and about

2 millims. from the poles it reduces to about 400 metres/second, which is not very different from the velocity of sound in air at the ordinary temperature. It is well to realise this, for it shows that the sound-wave which is produced by the spark has moved outwards through a distance of a few millimetres only by the time the metallic molecules have reached the centre of the spark.

In order to see whether the capacity of the jars and distance between the poles have an appreciable effect on the result, the displacements of the zinc lines were measured for sparking distances of approximately .5, 1.0, and 1.5 centims., and in each case the capacity was altered by taking the discharge from 2, 4, and 6 jars. Table II. embodies the result; the velocity (V') given being, as above explained, the average speed between the pole and a point at a distance of 2 millims. from it.

TABLE II.—Average Velocity (V') in metres/second of Zinc Molecules.

Sparking distance.	Wave-length.	Number of jars.		
		2	4	6
centims.				
.51	4925 (α)	814	556	416
	4811 (β)	1014	668	529
1.03	4925 (α)	400	499	415
	4811 (β)	501	548	545
1.54	4925 (α)	723	1061	435?
	4811 (β)	1210	1526	492?

The first striking fact shown by the table is the uniformly slower speeds derived from the doublet at 4925 as compared with that of the least refrangible line of the adjoining triplet, and we have assured ourselves that there is no difference in displacement between the two first components of the triplet. The third component is too weak and too near an air line to admit of satisfactory measurement. It was one of the main objects of our investigation to discover, if possible, such differences in the velocities as might indicate the presence of different kinds of molecules, but we hesitate to ascribe the differences found to such a cause. The line 4925 is the least refrangible component of a double line, which is wider and much stronger at the base than in the centre of the spark. In order to measure the displacement, the cross wire of the reading microscope has to be set on the edge of the displaced line, first near the pole, and then on a corresponding point nearer to the centre of the spark gap. Where the line is strong, the edge of the line would be the least refrangible edge of the *least* refrangible component, but when the line is weak, the strongest part of the line would be that part where the two components begin to overlap, *i.e.*, the

edge of the *most* refrangible component, and there would be a tendency to setting the microscope on the strongest part of the line rather than on the edge of it. It is easily seen that an error would be liable to arise, giving too great a displacement or too small a velocity. We are not at all certain that if this source of error were eliminated the double line would not show higher rather than lower values for the velocity, and hope to decide this question by using greater dispersion.

Comparing different capacities with each other, we find that for the spark gap of 5 millims. the velocities are greater for small than for large capacities; we offer at present no explanation of this unexpected result, which requires confirmation and further investigation. When the sparking distance is increased to 1.5 centim., the course of the sparks becomes so erratic that not much importance can be attached to the figures. A query has been attached to those that are specially doubtful. On the whole, there seems a tendency towards greater velocities in this case.

Our normal spark gap of 1 centim. does not show any decided difference due to capacity, and with our normal capacity of six jars the spark gap does not seem to affect the result. Hence we are justified in thinking that under the conditions named a reliable comparison may be made between the velocities obtained for different metals.

We have collected in Table III. the velocities V and V' as measured on our photographs. The results are nearly always the mean of two sets of measurements from different photographs. In some cases, such as magnesium, iron, manganese and silver, no satisfactory measurements could be made. The spectrum, as it appears on our films, does not always give the same distribution of intensity among the lines as is shown by the spectra of sparks taken with an induction coil and jars of small capacity, and it differs also, of course, from the arc spectrum. A discussion of the peculiarities of our spectra lies outside the range of this paper, and must be reserved for another occasion, but in the following account some of the chief features of our spectra are shortly pointed out. The metals are arranged in order of atomic weights.

TABLE III.

Metal.	Wave-length.	V' (metres per second).	V (metres per second).
Aluminium	4512 (α)		
	4478		
	4446	18901	13001
	3613 β		
	3602		
	3585		
Zinc	4925 } (α)	415	406
	4912 }		
	4811 } (β)	545	524
	4722 } (γ)		
Cadmium	5379 } α	435	472
	5339 }		
	5086 } β		
	4800 } γ	559	515
	4416 } δ		
	3613 } ϵ		
Bismuth	5209 } α		
	4561 } β	1420	1480
	3696 } γ		
	4302 } δ	533	488
	4260 } ϵ		
	3793 ζ	394	270
Mercury, from Cadmium Amalgam	5461 } α		
	4359 } β	988	550
	3663 γ	590	406
" from Zinc Amalgam . .	4359 β	481	
	3663 γ	383	

Magnesium.—In photographs taken on a stationary film we note the complete absence of the triple line in the green, which forms a prominent feature of the magnesium spectrum under ordinary conditions. The whole energy of the spectrum seems to be concentrated into the line at 4481 (α), which is exceptionally strong, and into the triplet beginning with 3838.4 (β), which appears as a doublet in our films, the two last lines probably not being resolved. A strong line seen both in arc and

ordinary sparks at 4703 is also absent. When the spectrum is photographed on the rotating film, the lines resolve into remarkable clouds (fig. 20, Plate 10), which do not admit of measurement. The appearance of the lines shows, however, that the velocities of the magnesium particles is great, and approximately the same as that of aluminium.

Aluminium.—The prominent lines are the two triplets beginning with 4512 (α) and 3613 (β) respectively, and the doublet which lies between H and K. The former do not appear in the arc spectrum, which shows the violet doublet strongly. The velocities we have obtained are the largest we have measured, but the displacements (fig. 21, Plate 10) are very small, and the lines are measurable only near the poles, so that the numbers are doubtful. The violet triplet seems displaced through a greater distance than the blue, but the measurements are so uncertain that we have taken the average displacement without distinguishing between them. The violet doublet almost disappears in the rotating film, leaving only a faint cloudy formation similar to that shown in the magnesium spectrum, but possessing peculiarities which require further investigation.

Manganese.—Many lines of manganese appear on our stationary photographs, but on the rotating film they completely disappear under the usual conditions of our experiments. When the slit is widened and the speed reduced, the displacements could be observed, but were not measured.

Iron.—The iron lines were not well marked, and completely disappeared in the rotating films.

Copper did not show any well-marked lines, the displacements of which could be measured.

Zinc.—This metal has already been discussed in detail, and it only remains to mention that the line at 4058 (ϵ) disappears on the rotating film.

Silver showed no prominent lines when our battery was discharged through it, but the calcium lines are always seen (see p. 212).

Cadmium.—A number of cadmium lines appear on our photographs, which agree in position with the lines so frequently measured; but there is some difference in the relative intensities as noted by different observers. The double line 5379 and 5339 (α) shows a greater displacement than that of the other lines, and the distance between the components is so great that the explanation given for the corresponding zinc lines does not seem to hold here. Fig. 22 shows the behaviour of the cadmium lines.

Mercury.—Sparks were taken from a surface of liquid mercury, and, though the displacements can be readily seen (fig. 23), and the edges of the lines are fairly sharp at some distance from the electrode, they are so diffuse in close proximity to it that no satisfactory measurements could be made at points corresponding to those taken in the case of other metals. Better results were obtained when the electrodes were either amalgamised zinc or cadmium; but the measurements in these cases, though they are given in the table, are difficult to make and cannot be trusted. When cadmium amalgam is used (fig. 24), the photographs show clearly that the mercury

line 3663 (Hg, γ) is parallel to the cadmium line 3613 (Cd, ϵ), and the measurements are fairly consistent, but when the pole was zinc amalgam, the displacements of the mercury lines seemed decidedly greater than that of the zinc lines. This would indicate a higher velocity for zinc than for cadmium molecules, while our previous results had given almost identical values for the displacements of the zinc and cadmium lines. There is here some contradiction which requires clearing up by further experiments.

Bismuth (fig. 25, Plate 11) gave us most interesting results, as it possesses some lines, such as γ , which are curved so little that the velocities of the molecules giving these lines is found to be larger than that observed in any other case except aluminium. On the other hand, the line at 3793 (ζ) indicates the smallest velocity measured. There are some special difficulties standing in the way of the measurement of the bismuth lines, which made us hesitate some time before definitely asserting the different curvature of the lines, but we think that our best photographs, one of which is reproduced in fig. 25, leave no doubt on the question. One of the difficulties lies in the fact that bismuth and mercury are the only metals in which the lines are repeated, owing to the oscillatory discharges. When six jars are in circuit, the appearance is that of fig. 26, and the lines become mixed and difficult to measure. Another difficulty lies in the great difference in the sharpness of the lines even on the stationary film, the lines which show a small curvature being much sharper. There was a possibility of an illusion due to this cause, similar to that explained in the case of the double zinc lines, but we cannot believe that the difference in curvature between the lines marked (γ) and (ζ) in fig. 5 can be due to this cause.

[April 26.] We possess very few investigations on the spectrum of bismuth. LECOQ DE BOISBAUDRAN, who is acknowledged to have purified his substances with extreme care, gives the line 5209 (α) as one of the characteristic lines of bismuth, and he also gives 4302 (δ) and 4260 (ϵ) as belonging to bismuth. The relative intensities of the lines as given by him cannot be expected to coincide with our own, as he used very different spark conditions. Our spectrum agrees, on the other hand, perfectly with that given by HARTLEY and ADENEY,* who traced no coincidence between the lines we made use of in this research with those of other metals.

As the great difference in the molecular velocities suggested the possibility that bismuth was a mixture of elements, we obtained, through the kindness of Messrs. JOHNSON and MATHEY, samples of bismuth prepared from three different sources. The visible portion of the spectrum was examined with great care, but no difference in the relative intensities of the lines could be detected.

6. Discussion of Results.

When we compare together the results obtained for different metals, the first question that arises refers to the connexion between the velocities and atomic weight,

* 'Phil. Trans.,' vol. 175, p. 130, 1884.

or rather vapour densities. Dr. FEDDERSEN was led by his researches to conclude that the spark through air volatilised the metal, which afterwards, according to him, took no further part in the discharge. If that is the case the process of molecular diffusion should, at equal temperatures, be inversely proportional to atomic weight. There is no doubt that the first luminosity of the discharge is entirely due to the spark breaking through the air. The air lines are so little widened in our photographs that it is only close to the pole that any metal vapour can be present while the air is luminous. During the interval between the initial current and the first return, the metal vapour will diffuse chiefly, if not entirely, by reason of the molecular velocities. The initial discharge starts a sound-wave which must leave for a short time the air between the electrodes in a state of rarefaction, and it is perhaps right to consider that the mass of metallic vapour suddenly formed is driven by its own pressure into the partial vacuum formed by the heated air. It would seem more correct, therefore, to compare the process with that of a gas under pressure flowing into a vacuum than to that of pure thermal diffusion. There is not much difference between these views, and we may take it that in our experiments we have approximately measured the velocity of sound in the metallic vapour. This gives a relation between its temperature and density. Neglecting a possible difference in the ratio of specific heats, the relation

$$V = 80 \sqrt{T/\rho}$$

should hold approximately, T being the absolute temperature, V the velocity of sound, and ρ the vapour density referred to hydrogen. Thus, for cadmium, the average molecular velocity found was 560, and substituting $\rho = 56$, we obtain $T = 2700$, which seems a possible but rather low value. We must conclude that the molecule of cadmium in the spark cannot have a mass which is much smaller than that determined directly near the boiling point of the metal.

If we compare different metals with each other we are struck with the almost identical numbers obtained for zinc and cadmium. It is possible, of course, that zinc vapour may be diatomic, but it seems more probable that as the spectrum of zinc and cadmium show homologous lines, the molecular constitution of the two vapours is the same. Aluminium, with a small atomic weight, has a high velocity, and so has magnesium, but the ratio of the velocity of aluminium to cadmium is roughly as 3 : 1, while the ratio of the square roots of the atomic weights is only as 2 : 1.

The uncertainty of our numbers is so great that we only wish at present to draw the general conclusion that the two metals having the lowest atomic weights, which have been examined by us, are also those showing the highest velocities. For the same reason we forbear discussing the question as to the different behaviour of different lines, especially with regard to other peculiarities possibly existing in the behaviour of lines which show abnormal velocities. The data are at present too scanty and uncertain to allow us to attach any value to the coincidence of such peculiarities.

An interesting question arises as to whether, in the case of an alloy, the different components affect each other or not. The evidence, so far, goes to show that they do; the zinc lines, for instance, are less curved when the zinc is amalgamated, and similarly when electrodes of bismuth are moistened with calcium chloride the displacement of the bismuth lines is reduced.

7. *Experiments without Prismatic Decomposition.*

Dr. FEDDERSEN took photographs of the entire spark by means of the revolving mirror, and the appearances he obtained were very irregular, though his experiments allowed him to draw some general important conclusions. We considered it to be of interest to take some photographs after removal of the prism, retaining the slit; fig. 29 (Plate 12) shows the appearance with zinc poles under the normal condition of our experiment, *i.e.*, with the six jars and a pole distance of 1 centim. The straight luminous initial discharge which passes the air gap is followed by a number of curved lines, which represent the oscillatory discharges. Fig. 30, in which the oscillations are spread out by the interposition of self-induction, gives a better representation of the phenomenon. We notice, in the first instance, the alternation at each pole between strong and feeble discharges: the strong discharge at one pole being opposite a weak discharge at the other. This peculiarity was pointed out already by Dr. FEDDERSEN. Our experiments do not allow us to decide at which pole the discharge is most luminous, and it would be important to find this out, as it would allow us to decide whether the discharge through the metal vapour resembles more that of a vacuum tube or that of the voltaic arc. Fig. 30 shows the initial discharge to be followed by a second straight luminous band before the curved lines begin. The curvature is irregular, and the two poles do not behave exactly alike.

The distance between successive discharges is the same for all metals we have tried, which shows that the resistance of the metal vapour cannot be a dominating portion of the whole resistance, for doubtless different metal vapours will differ in resistance, especially as they must be present in very varying quantities, owing to differences in volatility. As we can count about ten discharges, we may take it that the damping is small and therefore the time of an oscillation $2\pi\sqrt{LC}$, if L is the self-induction. From this we calculate that our self-induction was about 3000; for steady currents a rough estimate of our circuit gave a self-induction of 1000, and we know that for rapid oscillations it must be greater. If we adopt the higher number, we may further conclude that the total resistance of our circuit must have been small compared to 20 ohms, while, taking the lower estimate for the coefficient of self-induction, the resistance was small compared to 12 ohms, a further proof, if one were needed, of the fact that once the insulating property of air is broken down, its conductivity may be large. We do not wish to enter further into some interesting

questions connected with this matter, as we are only concerned with the bearing of our experiments on the main subject of our research.

The curved lines of the oscillatory discharges may serve as a basis for the calculation of the molecular velocities, and if this is done, higher values are obtained than those we have derived from our experiments with the complete apparatus. Aluminium and magnesium gave again, however, the highest velocities near the pole, but that of the zinc molecules exceeded considerably the velocities found for cadmium.

There is here, however, a considerable difficulty in the interpretation of the result, as without the prism it is impossible to separate the different lines, and, what is perhaps more important, we do not get the effect of the first discharge at all, as that is hidden behind the dense luminous column of the straight air discharge.

If a photograph be taken of the spark on the rotating film, the image is always drawn out most near the middle of the spark, and we obtain images such as fig. 31. It is not quite easy to see why the metallic particles should remain luminous in the centre of the spark longer than near the pole, unless there is some inflow of cold air from the poles inwards. Such an inflow might be produced through the effects of rarefaction produced by the initial heating of the air by the spark.

8. *Sources of Error.*

Different photographs, obtained exactly in the same way, sometimes differ considerably in the value they give for the molecular velocity, and there is little doubt that the chief cause of error lies in the fact that the discharge is not a straight line parallel to the slit, but takes place in irregular curves, and, as appears already on Dr. FEDDERSEN's photographs, the successive oscillations of the same discharge take sometimes very different courses. When we first began to work we used smaller capacities, and our results were more irregular, because the course of the discharge was more erratic. The large capacity acts in the direction of making the path of the discharge straighter, unless the sparking gap becomes too great. If the molecular stream is a straight line, our calculations are based on the further assumption that the image of the point of divergence falls exactly on the slit. If that point is at a distance h , measured perpendicularly to the slit, the molecules would have to traverse a distance $\sqrt{y^2 + h^2}$, if the projection of the distance along the slit is y . Calling V the velocity of the molecular stream, v that of the photographic film, it follows from $x = Vt$ and $vt = \sqrt{y^2 + h^2}$ that

$$V^2x^2 - v^2y^2 = h^2v^2.$$

x and y are proportional to the coordinates of the spectroscopic lines as measured on the film, and the curve represented by the equation is a hyperbola.

The error introduced is such that a constant velocity would appear as one infinitely large close to the pole and gradually diminishing. If h is small, the hyperbola would soon coincide with its asymptote, and in that case the error in the molecular velocities

as deduced from points which are not in close proximity to the poles, would not be large. Some of our photographs give evidence of being affected by this error.

Other inaccuracies which cannot readily be evaluated are introduced by the curvature of the spark. If we imagine the molecular streams to follow the course of the spark, the appearance on our photographs might be considerably modified. In particular, if the curvature lies in a plane passing through the slit, the molecules near the pole will move towards the slit or away from it, and the components of the velocity resolved along its direction will have a smaller value than near the centre of the spark, where its direction is nearly always parallel to the slit. The error introduced is in a direction opposite to that found in the previous case, the molecular velocities near the poles now appearing too small.

One further point remains to be noted. Photographs like those illustrated by fig. 29 and fig. 30 cannot be easily explained, unless we take it that the metallic molecules actually carry the electric current. If that is the case, and if the process of discharge is similar to that advocated by one of us in 1882* and now generally accepted, the molecular stream will carry with it the ionic charge, at any rate in the positive part of the discharge. Now, considering successive oscillations, electric forces must continue to act on the metallic molecules, first accelerating, then retarding, and then again alternately accelerating and retarding. Under the conditions of our experiments, and with the velocities measured by us, the molecules would only have got to a distance of about 1 millim. from the pole before the second acceleration takes place. If that is a correct view, we should expect a sinuous curve for the molecular path, and there seems indeed a tendency towards such a form in some photographs, as for instance that given in fig. 22. The only way to overcome this complication will be to increase the period, so that we may be able to measure the velocity of the stream separately for each oscillation. The effect of magnetic forces on the velocity of the stream may also supply useful information.

9. *Effect of Self-Induction in the Spark Circuit.*

In the course of our investigation we were led to insert a coil of wire into the spark circuit in order to separate the oscillatory discharges. We discovered in this way a curious effect on the appearance of the spectrum, the air lines completely disappearing when the coil was inserted, provided the self-induction was sufficient. The most plausible explanation seems to be that the air lines are produced entirely by the first initial discharge, when the spark gap contains no metallic vapour. The subsequent oscillations pass, on the contrary, through the metal vapour, which in the meantime has had time to diffuse away from the electrodes. By inserting the coil, the initial discharge takes place more slowly and apparently does not heat up the air sufficiently to yield the line spectrum. The whole duration of the spark is considerably lengthened, and the

* 'Bakerian Lectures,' 1884 and 1890; 'Roy. Soc. Proc.,' vol. 37, p. 317, 1884, and vol. 47, p. 526, 1890.

discharge may pass through the metal vapour, which after a few millionths of a second fills the whole spark gap. The spectrum is modified by the change in the mode of sparking, and Mr. HEMSALECH is at present investigating this change, but our joint photographs are sufficient to show that the spectrum is *not* reduced to that of the arc discharge, the double zinc line at 4925, even with large self-inductions, remaining strong, though it thins out a little. We consider the method of investigating spectra a most useful one, and it allows us to distinguish at once what is an air line and what is not. The obnoxious noise of the spark is also much diminished.

[April 26, 1899.] Professor KAYSER has kindly drawn our attention to a paper by Mr. AUER v. WELSBACH ('Wiener Sitzungsberichte,' 88, II., 1883), in which an interesting device is described by which strong spark spectra may be obtained without the usual induction coil. It is essentially an arrangement by which the spark at the break of the primary current is used in place of a gap in the secondary circuit. The air lines also disappear under these conditions. In how far the spark is of a similar nature to that used by us is difficult to say without direct comparison of the spectra obtained.

When the above method is applied to different metals, it is found that the calcium lines H and K of the solar spectrum appear in most, possibly in all, cases. There is perhaps nothing surprising in this, owing to the presence of calcium in the dust of the air, and the probability of its occurring as an impurity in many metals. But what is surprising is the great intensity of these calcium lines, as compared with those of the metal proper when the poles used are silver. We deposited some of the metal electrolytically, and Mr. J. CROWTHER fused the deposit into poles on a block of willow charcoal, which contains only a very small amount of ash, but we must admit the possibility of some traces of calcium having been taken up by the silver in the process.

The silver so prepared gave not only the H and K lines, but also the line at 4226, with undiminished vigour. We do not offer any explanation as to the possible sources of calcium, either in the metal or in the dust of the air, but the fact is rendered remarkable by the appearance of the lines in question when the spectrum is taken on the rotating wheel. Fig. 27 is a photograph taken on the stationary film without self-induction, and the H and K lines are seen strongest near the centre of the spark. With self-induction, the strongest lines of the spectrum are those of calcium. In fig. 28 the disc was spinning, and there was no self-induction. The lines H and K present a comet-like appearance, K being much the strongest. The head of the curve corresponding to the K line is displaced towards the violet, and if our interpretation of these curves is correct, the photograph seems to prove that the H and K vibrations start not at the pole, but in the centre of the spark, and luminosity begins not when the main initial discharge strikes through the air, but, roughly speaking, about the 200,000th part of a second afterwards, when the luminosity of air as shown in our photographs has completely

ceased. Further experiments are in progress, and the matter is only mentioned here because any one repeating our experiments on the influence of self-induction will be struck by the intensity of the H and K lines when the spark is taken from silver poles. The extraordinary persistency with which the slightest trace of calcium is known to give the lines in question renders any investigation on the actual source of the calcium present very difficult. The effect of polishing, which was necessary to obtain good sparks, undoubtedly results in calcium contamination, as we were able to ascertain by experiment, but silver poles carefully prepared and not brought into contact with any foreign material, but polished by friction against each other, still gave the H and K lines very prominently.

10. *Conclusion.*

We point out in conclusion the principal results arrived at in the preceding investigation.

We do not consider that the numbers arrived at for the molecular velocities can lay claim to great accuracy, owing to the irregularities in the results, some of which have not quite been traced yet. But we think that we are able to say generally that metals of light atomic weight, like aluminium and magnesium, are projected from the poles with greater velocities than the heavier ones we have tried, such as zinc, cadmium and mercury. Different curvatures of different lines are marked in the case of bismuth, and are not easily explained, except by assuming the presence of different kinds of molecules having different masses, the lighter ones diffusing more quickly. We have thus established a method which is likely to prove of extreme value in separating the effects of different molecules.

Our experiments also allow us to draw another important conclusion. When two lines of a metal are of unequal intensity, it is not always due to the fact that at any period of the discharge the vibrations which appear the strongest are really the most intense. Our eye or the photographic film only perceives the total energy sent out, and the time of luminosity is in many cases very different for different lines. A vibration which is weak but persists may appear stronger than one of greater intensity which only appears for a very short time.

We have been led in addition to a new method of taking spark spectra with an induction coil, by the discovery that self-induction in the spark circuit leads to the disappearance of the air lines, which are often very troublesome in the investigation of spark spectra.

Finally, the appearance of the calcium lines in the photograph of the silver spectrum has shown the existence of a new type of spectroscopic lines, namely, one that starts in the centre of the spark and is propagated towards the poles.



Fig. 3



Fig. 4

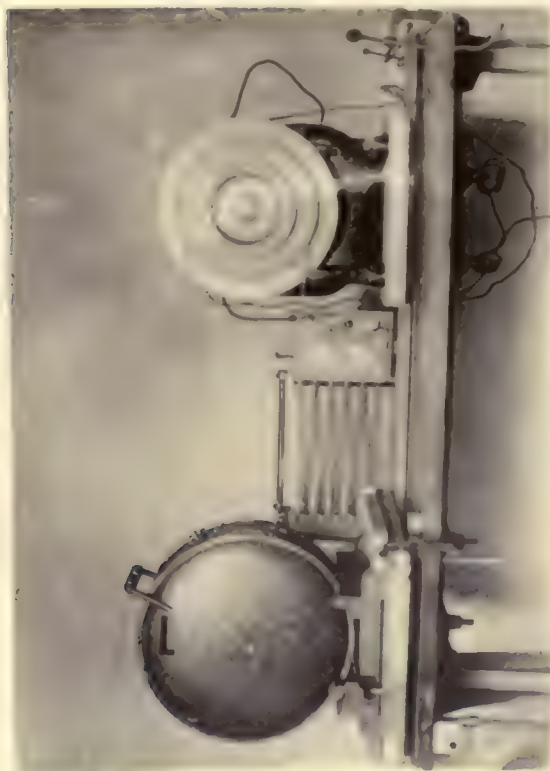
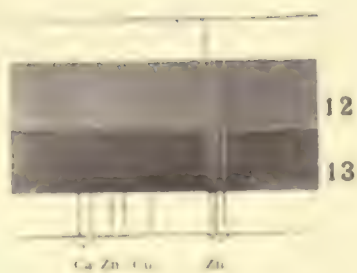


Fig. 5





11



14



15

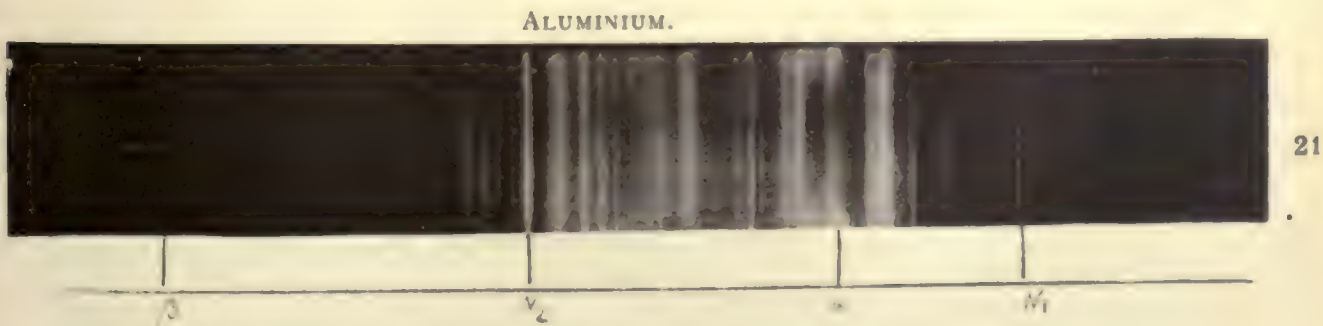
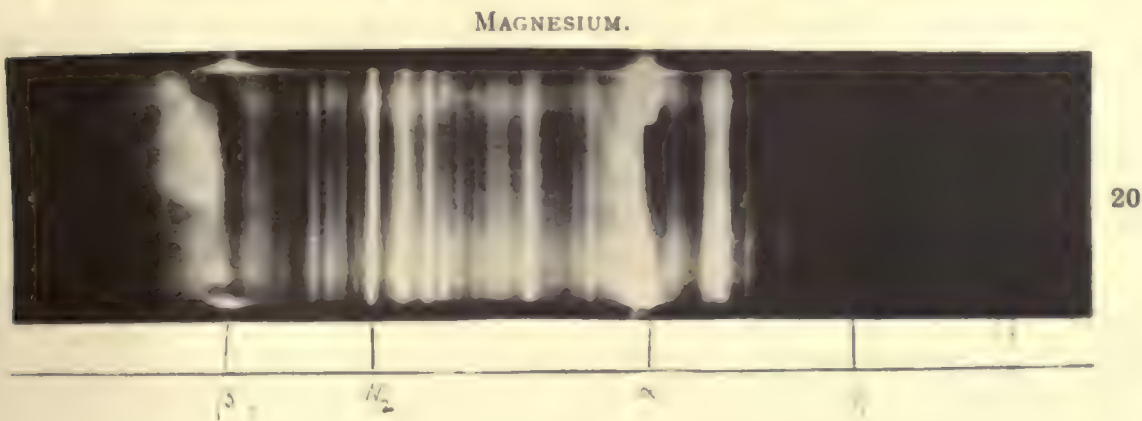
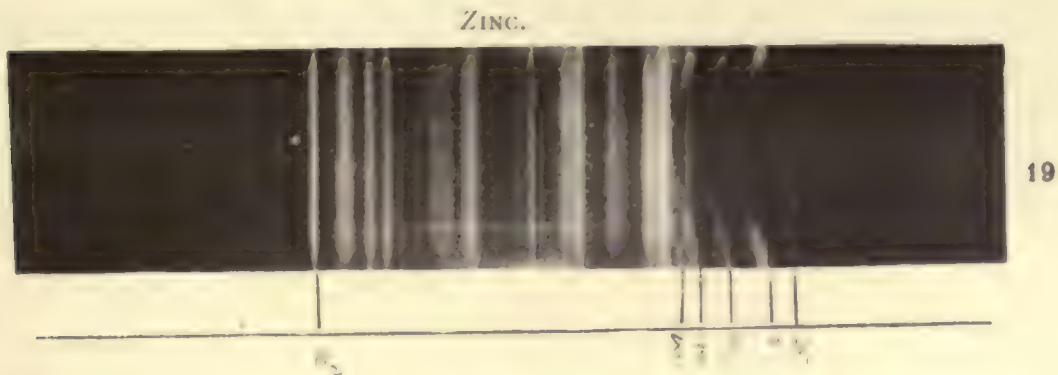
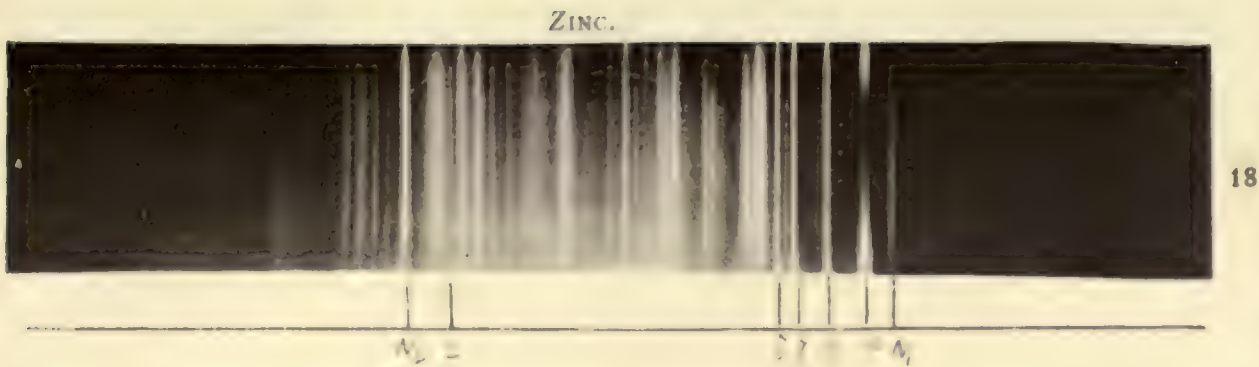


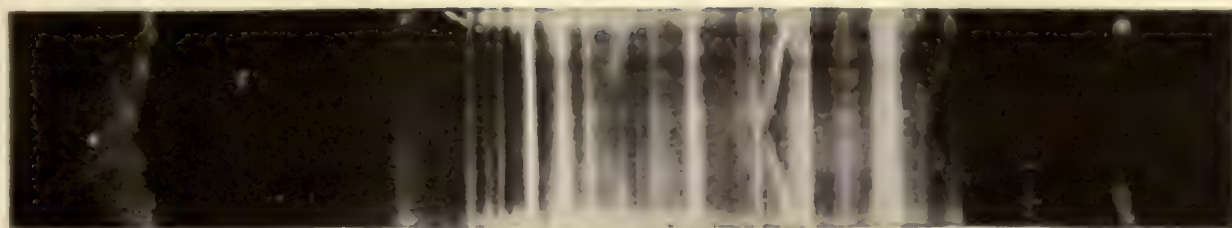
16



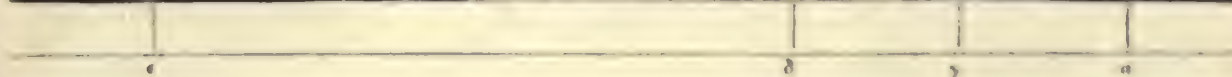
17







22



γ

S_2

β

S_1

α



23

Upper Pole Mercury, Lower Pole Zinc.

Cd Hg

ϵ

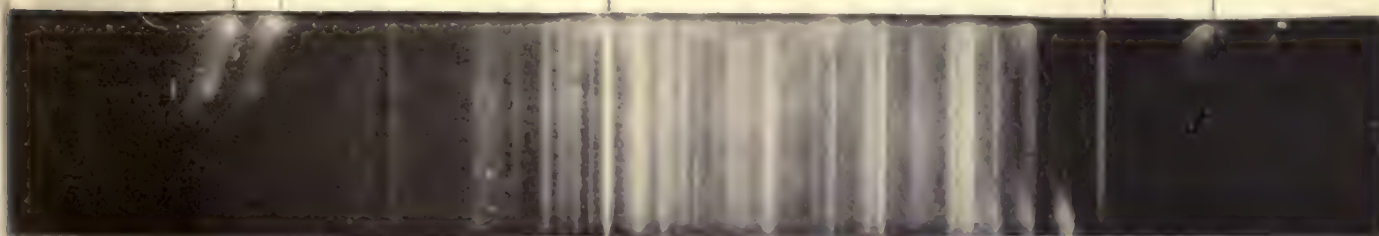
γ

S_2

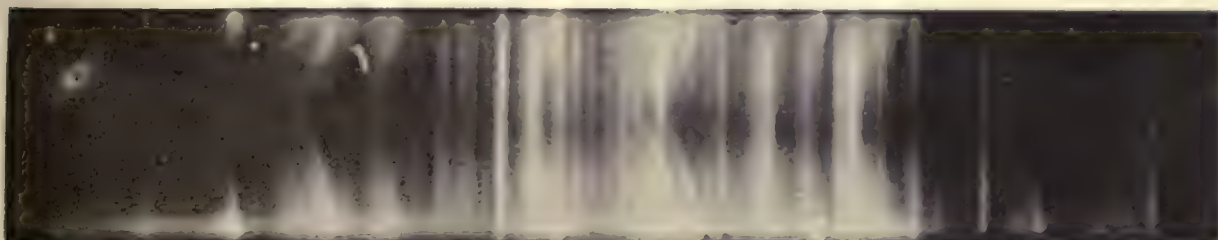
S_1

Hg

α



24



25



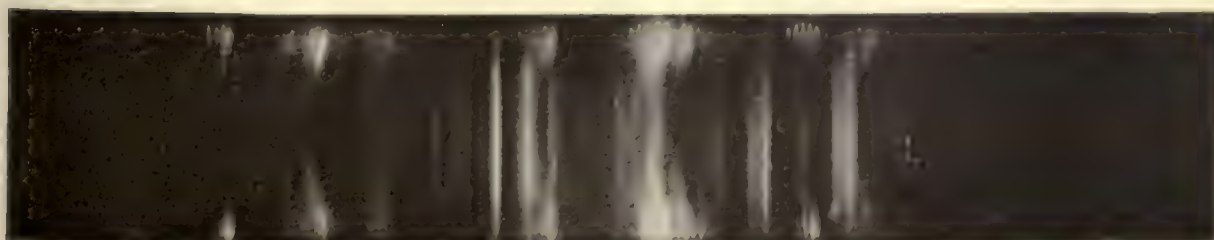
γ

ϵ

δ

β

α



26

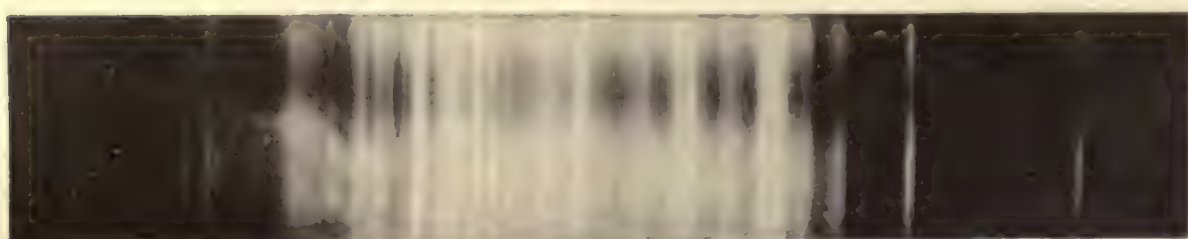
SILVER.



27

K H

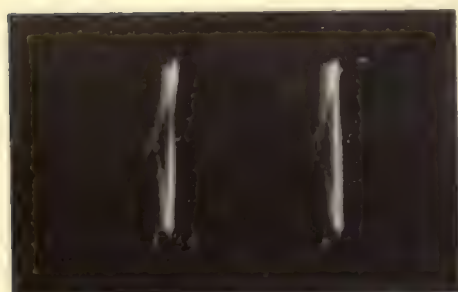
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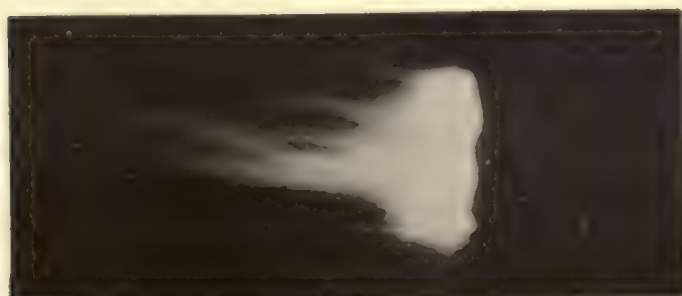
28

K H

29



30



31

VII. *On a Quartz Thread Gravity Balance.*

By RICHARD THRELFALL, *lately Professor of Physics in the University of Sydney,*
and JAMES ARTHUR POLLOCK, *Demonstrator of Physics in the University of*
Sydney.

Communicated by Professor J. J. THOMSON, F.R.S.

Received, April 11,—Read, April 27, 1899.

[PLATES 13, 14.]

THE problem of replacing dynamical by statical methods of studying the variations of the earth's gravitational force has long occupied the attention of astronomers and physicists, and a good many attempts have been made to construct an instrument which should enable relative measurements of gravitational force to be carried out with a smaller expenditure of time and trouble than is incidental to the observation of pendulums.

The only kind of force which is practicable as a means of opposing gravitation in the construction of such an instrument as is here contemplated, is that derived from the elastic properties of matter.

Accordingly the problem is reduced to that of constructing either a spring balance of sufficient accuracy, or of making use of the elastic properties of a gas.

In both cases, when we approach the limits of accuracy obtainable by pendulum observations, we have to face very great difficulties arising from the necessity of ascertaining the temperature of the apparatus within very narrow limits, and this obviously implies the even greater difficulty of insuring that the apparatus shall have the same temperature at every point.

If we add to this the consideration that the apparatus must be reasonably portable, and of such construction that it is not possible to disturb its mechanism by the shaking inseparable from transport, it is evident that we have to face a mechanical and physical problem of considerable difficulty.

Until Mr. Boys discovered the unique properties of fused quartz, in 1887,* no material having elastic properties of the requisite simplicity and constancy was available, and from this cause, if from no other, all attempts at constructing a statical instrument of reasonable accuracy must necessarily have failed—as they all did. But even setting this aside, we are satisfied that all the designs—some of them of great

* 'Phil. Mag.,' June, 1887, p. 489.

ingenuity—which have hitherto been submitted, must necessarily have failed from the difficulty of securing in them the requisite uniformity of temperature.

With regard to forms of apparatus in which advantage is taken of the elastic properties of gases, it is proper to observe that, though it is possible to arrange a compensation effective to the first order of the variations due to change of temperature, yet the apparatus must almost necessarily be too large to satisfy the condition as to the temperature being sufficiently uniform throughout.

Very closely associated with the problem above discussed is that of making an instrument by which small secular variations in the gravitational force at any one place may be ascertained, though in this case the problem is very considerably simplified, because the question of portability does not arise, and arrangements may be made for minimising fluctuations of temperature. In this case, however, the observations should be of a higher order of accuracy than is necessary during a gravity survey.

As soon as we became familiar with the properties of fused quartz, it became obvious to us, as well as to others, that by taking advantage of these qualities it might be possible to construct a balance having sufficiently permanent elastic properties to give a practical solution of the problem of constructing a gravity meter.

A committee of the British Association, which in 1886 had invited designs for a gravity meter, reported in 1889 that work had been suspended pending a trial of fused quartz. Our own attempts to construct a gravity balance began in September, 1889, and have continued uninterruptedly ever since.

When we began to work at the matter we formed an impression that the problem of observing small variations in the intensity of gravity at any one place would prove simpler than that of constructing a portable instrument, and consequently we first turned our attention in this direction. We worked at instruments of what may be called the non-portable balance class for two years, at the end of which time we had satisfied ourselves that we were not likely to attain to sufficient sensitiveness, and accordingly we turned our attention to the construction of a portable instrument. We experimented in this direction for some time, with the result that in October, 1892, we began to construct what we hoped would prove to be a final form of instrument, but it was not until September, 1893, that we had got it forward enough to commence systematic observing.

With regard to portability we may say that we have travelled with the present balance over 6,000 miles. Of seven quartz threads which we have had in actual use since the balance was completed in September, 1893, only one has broken. During the first journey in February, 1894, and through the negligence of a person who had undertaken to look after it, the balance was knocked off its stand and practically destroyed; the only part which was not broken was the thread. The present thread was mounted on the 10th of September, 1896. It has travelled over 4,600 miles by cart, railway, and steamer. Observations have been taken with this thread at four

stations in New South Wales, at Melbourne in Victoria, and at Hobart and Launceston in Tasmania. On November 23rd, when hurrying to catch the train at Springwood, N.S.W., one of the handles of the box containing the balance broke, and one end of the box fell through a distance of about two feet on to the asphalt platform. The reading was found to be altered when we got to Sydney, but the thread was undamaged. As the final result of the present investigation we have determined the value of "gravity" at Hornsby, a station 21 miles from Sydney and 472 feet above the laboratory, relatively to that at Sydney, in three journeys, with a maximum difference less than one part in 500,000. For the purpose of a survey the evidence shows that a single observation with the balance will enable g to be determined relatively to a standard value to within one part in 100,000. There is a great probability, however, that the error would be less than one part in 200,000.

Before proceeding to the discussion of the subject of this paper we desire to perform the pleasant duty of thanking those who have assisted us in one way or another, and first amongst these is Mr. JAMES COOK, F.R.A.S., our mechanical assistant. Mr. COOK made the whole of the instrument, except the thermometric appliances, including his own working drawings from our sketch designs. It is not too much to say that had we not been so fortunate as to have commanded his great mechanical skill and accuracy we should in all probability have failed in our undertaking.

To Mr. J. J. E. DURACK, Deas Thomson Scholar of the University of Sydney, and to Miss FLORENCE MARTIN, we owe our thanks for much observational assistance. Through the enlightened liberality of the Commissioners of the Railways of New South Wales we were provided with free passes over the government railways. To them, and to the Secretary for Railways, Mr. HUGH MACLACHLAN, we desire to tender our thanks, not only for our free passes, but for the unfailing kindness and courtesy which they showered upon us.

Amongst those who have assisted us with advice upon special points we desire especially to thank our colleague, Professor GURNEY, Mr. G. H. KNIBBS, Mr. E. F. J. LOVE, Mr. G. F. FLEURI, M. GUILLAUME, Mr. GRIFFITHS, and Mr. CHARD, L.S.

During our journeys we were provided with facilities for making our observations by Professor LYLE, of the University of Melbourne; Professor MCAULAY, of the University of Tasmania; Mr. ALEXANDER MORTON, Curator of the Tasmanian Museum at Hobart; Mr. W. J. BAIN, of Launceston; Sir PHILIP FYSH, (late) Premier of Tasmania, and Dr. WIGAN, Acting Mayor of Armidale in 1897.

The Surveyor-General of New South Wales also deserves our thanks for having placed a disused theodolite at our disposal, the circle of which was employed for a long time as part of our balance.

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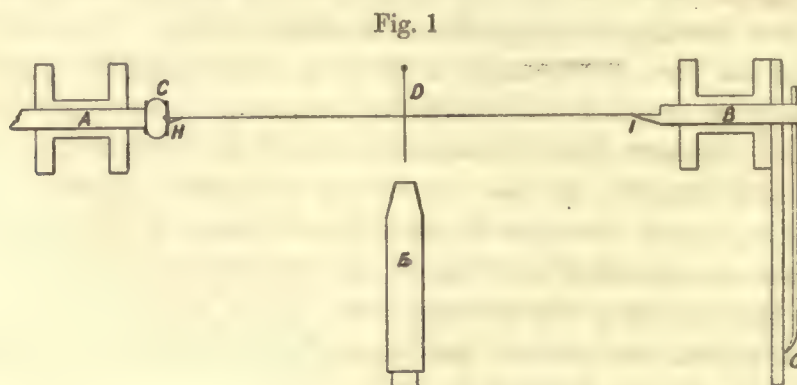
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GENERAL DESCRIPTION OF THE INSTRUMENT AND PRELIMINARY REMARKS.

A and B (fig. 1) are two metallic rods capable of adjustment by sliding along their common axis, but having no freedom to move transversely; in our earlier experiments we made use of the head stock and back centre of a watchmaker's lathe.



C is a coach spring attached to A, and carrying a point H, to which the end of the quartz thread is fastened.

B is a brass axle capable of turning about the axial line HI, which also represents the quartz thread; it is attached rigidly to an arm carrying a vernier G. The vernier moves over a divided circular arc—a sextant being in fact employed.

The quartz thread has as nearly as possible a diameter of $\cdot 0015$ inch = $\cdot 0038$ centim., and is very uniform; it is soldered up to the points prepared for it at H and I.

The distance of A from B is regulated so that the thread is stretched tight by the spring at C.

The length HI is 30.5 centims.

D is a piece of gilded brass wire 5.3 centims. long, and its mass is 0.018 gram; it is attached to the thread by soldering, the thread lying in a little kink in the wire.

It is adjusted so that its centre of gravity lies a little to one side of the thread.

E is a microscope attached to the frame of the machine so as to occupy an invariable position with respect to the supports A and B.

The microscope is provided with a riding level showing 2" of arc per division of 2.5 millims. at ordinary temperatures.

The whole apparatus is provided with levelling screws, so that the axis of collimation of the microscope can be brought into an invariable position by means of the riding level, which invariable position is very nearly or quite horizontal. Also the thread itself can be adjusted to lie in a horizontal plane by means of a subsidiary level, which is permanently attached to the frame work, and is at right angles to the riding level.

The apparatus is thermally insulated so far as possible, and a platinum wire thermometer wound upon very thin glass lies alongside the thread.

There is also an arrangement for arresting the end of the lever for security during transport.

The gravitational moment of the lever about the thread requires to be adjusted by the addition of small drops of fusible metal solder. The moment is so adjusted that about three whole turns of each end of the thread are required to keep the lever horizontal. This adjustment is made once for all; during the process of observing the thread is twisted from one end only, viz., the end attached to the sextant arm. It will be shown directly (in the section dealing with the theory of the instrument) that the equilibrium of the lever becomes unstable when its centre of gravity rises a few degrees above the horizontal plane passing through the thread.

The microscope is so arranged with respect to the lever that, when the riding level is horizontal, the image of the end of the lever lies on the cross wire; and the lever itself is almost, but not quite, in the position of instability.

By turning the vernier arm it is possible to increase or diminish the twist of the thread from I up to the lever. When the thread is increasingly twisted, the side of the lever on which is the centre of gravity rises until the position of instability is reached and the lever upsets; it is caught, however, by the arrester, and is not allowed to fall right over. When the intensity of gravitational force increases, the centre of gravity of the lever falls, and the thread has to be twisted by the vernier arm in order to bring the lever back to its former position.

The immediate subject of observation is the amount of twisting or untwisting necessary to bring the lever to its sighted position.

In order to calibrate the instrument, it is necessary to know the total twist of the thread, that the thread is uniform, or at all events of a definite shape, the position of the centre of gravity of the lever, and the exact position occupied by the lever with respect to the ends of the thread. As these quantities are not exactly ascertainable, we prefer to calibrate the instrument by observing the change of reading which occurs when it is taken from Sydney to Melbourne—the gravitational data of both of these places being sufficiently well established.

It appears from the theory below that this information, together with the vernier

reading at a third station and the corresponding temperature readings at each station, give us all the data necessary for calculating the value of gravity at the third station.

The necessity of observing the temperature arises from the fact that the rigidity of fused quartz threads increases with increase of temperature. The effect is, of course, complicated by the changes which take place in the dimensions of the threads. The nett result is that as the temperature rises the "stiffness" of the threads increases.*

The dimensions of the lever also change, and in such a manner as to partially compensate the changes of "stiffness" taking place in the thread. In the actual instrument the resilience as well as the figure of the coach spring vary with temperature, the line of collimation of the microscope may also vary relatively to the level, and the metal framework may also twist and vary in shape in any manner. All these effects are found to be capable of collection into a single temperature coefficient—which, so far, we have found to be sufficiently well expressed by a single term—the temperature scale adopted being the platinum scale of CALLENDER.

Many attempts were made to annul the effect of variation of temperature by constructing levers composed of two bars of metals of different expansibilities, an account of which will be found in the appendix, but all such attempts came to nothing.

The sensitiveness of the instrument is at present such that to compensate for a change of one part in 100,000 in the value of g it would be necessary to move the vernier arm through 2.12 sextant (doubled) minutes = 1.060 minutes of arc. Also a change of temperature of one-tenth of a degree alters the circle reading by 3.15 sextant minutes, gravity being invariable.

Although quartz is immeasurably superior to any other known material as regards the constancy of its elastic properties, it must not be supposed that it is entirely free from elastic defects. As a matter of fact, it is only just good enough for the present purpose. One of the great difficulties we have had to overcome has arisen from the fact that it is only by the most judicious choice of dimensions that it is possible to reduce the viscous yielding of the thread to within practicable limits, and even as it is, although the thread of the present instrument has been twisted for more than two years, and indeed purposely overtwisted for part of that time, we are still obliged to apply an important though practically constant correction on this account. In other words, the reading of the sextant arc is still slowly decreasing, and though the rate of decrease is now constant for all practical purposes, it has to be taken strictly into account in interpreting the indications of the instrument, even when consecutive observations are separated by an interval of time as short as a single day.

It will, no doubt, occur to the reader that we ought to use a finer thread, in order to get rid of this source of inconvenience. This, however, experience has shown us, we are not at liberty to do, for a finer thread means either a finer lever or one soldered to the thread at a point nearer to its own centre of gravity. The former

* THRELFALL, 'Phil. Mag.,' July, 1890.

solution is inconsistent with the necessity of having the lever strong enough to bear arresting without change of form, and the latter has the drawback that it tends to magnify the effect of such variations as do actually occur in the shape of the lever. In short, the design of a gravity balance becomes a matter of compromise just like any other engineering undertaking. In calculating the moment of the gravitational forces brought to bear upon the thread by the weight of the lever, it must not be forgotten that the effective weight is reduced in consequence of the flotation of the lever by the air surrounding it. At an accuracy of one part in a hundred thousand in the estimation of g the effect of variations of barometric pressure or humidity would become sensible, and it is therefore necessary to protect the lever against variations of air density. This is done by enclosing the whole apparatus in an air-tight casing within which the air is kept at a constant density. In practice the density selected corresponds to a pressure slightly below the minimum external pressure of the air. The apparatus must also clearly be filled with dry air to avoid the deposit of dew. As a consequence, the twisting of the thread necessary to afford a reading of the instrument, has to be carried out by means of a shaft working through a stuffing box; and the requisite accuracy in the estimation of the twist given to the thread makes it necessary that the rod shall work almost without friction in the stuffing box.

We have devised a sort of mercury and tallow joint which has got over the difficulty fairly well; and which is also applied to the stuffing box through which the rod of the arrester works.

An aneroid in connection with the internal space enables any leakage to be detected.

The constructional difficulties above indicated were further increased by our determination to have no iron or steel work about the machine: this was due to fear of magnetic interference; with which, however, we have never been troubled.

The degree of portability attained will be understood from the following statement of the sizes and weights of the various appliances requisite for an observation of gravity, as, for instance, during a survey when everything must be provided.

	Length.		Breadth.	Depth.	Weight.
	ft.	ins.	ins.	ins.	lbs.
Box containing balance	2	9 $\frac{1}{2}$	19	15 $\frac{1}{2}$	106
Box of resistance coils	2	4 $\frac{1}{2}$	10	10	23
Box of accessories	2	1 $\frac{1}{2}$	17 $\frac{1}{2}$	11 $\frac{1}{2}$	82
Legs of tripod stand	15
Total weight					226

The above weights and dimensions refer to a balance of gun-metal and copper, and accessories taken just as they came to hand from the laboratory. Both weights and dimensions might be greatly reduced if so desired. The weights certainly might be easily halved.

It is necessary to observe either upon a stone, cement, earthen or asphalte floor. Boards, however strong, do not form a sufficiently inelastic support.

INSTRUMENTAL DETAILS.

The drawings on Plate 13 are to scale, and ought to be self explanatory. Notes, however, have been added on the page facing the drawings in order to make it easier to follow the latter. It will be seen that the general principle of construction is as follows :—All the essential parts are rigidly held together by a system of bars forming a complete mechanism. This is then thrust into a tube of copper, which it fits precisely, and the tube of copper is further surrounded by a packing of paper to insure some degree of thermal insulation. The paper in its turn is surrounded by an outer tube of brass, and this is held down to the base by brass clips. The copper tube is closed at one end by the brass cover carrying the vernier arm and mercury stuffing box, which constitute the circle end of the machine. At the other end there is a smaller brass cover, through which projects the end of the arrester shaft and the end of the thermometer ; or, rather, the thick terminals and the end of the ebonite shank on which the glass tube is mounted. The aneroid tube also passes to the interior of the apparatus through this end.

The copper tube has two openings at opposite ends of a horizontal diameter, and into these openings are fastened, at one side a window, at the other the microscope focussed upon the end of the lever.

The under frame is provided with levelling screws so spaced as to fit the grooves of the top of a Kew magnetometer tripod. The instrument having been reconstructed several times does not now occupy the best position on the under frame, and this has necessitated the addition of a heavy lead counterpoise. Without this counterpoise the weight carried by the back levelling screw is too great to permit of the screw being turned with sufficient ease for exact levelling. The counterpoise is not shown in the drawing, but appears in the photograph (see Plate 14).

Attachment of the inner mechanism to the copper tube.—The bars connecting the bearing (which supports the “spring” end of the thread) to the bearing which carries the vernier arm are of gun-metal, and the bearing which carries the spring fits with considerable accuracy into the copper tube, carefully bored for the purpose. During our earlier observations the spring bearing was quite free to slide up or down the copper tube according as the temperature rose or fell. After one of our journeys, however, we thought that there was some evidence of the spring end of the thread having moved, and it appeared possible to connect this motion with the freedom of the spring bearing. Accordingly at present the bearing is wedged tight to the copper tube.

Stuffing Boxes.

The idea was to render the brass work incapable of being amalgamated by plating

it with nickel, which for ordinary purposes may be regarded as incapable of amalgamation. The fit of the shafts both of the vernier arm and of the arrester is made as good as possible without being at all stiff. The joints between the shafts and the cylindrical holes in which they work are further filled in with tallow. Outside a cup-shaped depression is arranged, and this is filled with mercury. As there is a partial vacuum inside the apparatus, the tendency is for the mercury to drive the tallow through the joint and then to follow it. The joint is very fine, however, and the surface tension of the mercury tends to oppose this motion. The practical result is that we obtain a smoothly working motion and a sufficient air tightness so far as inwardly directed air pressures are concerned.

Microscope.

The microscope is supported on a flange soldered to the thick copper tube. There is also a flange on the tube within which the microscope is fixed, and the adjustments of the microscope are partly made by sliding one flange over the other, the clamping screws which press the opposing surfaces together being passed purposely through holes much larger than the screw diameters. The flanges are ground to fit, and are put together with a little tallow for the sake of securing air tightness.

The microscope itself is an ordinary Zeiss microscope tube furnished with the "A" objective, giving a magnification of about 100 diameters. The adjustments are made as follows. It is required to adjust the microscope so that the image of the end of the lever will be sharply in focus, and bisect the cross wire when it is a small definite amount below its position of instability. For the purpose of arriving at this adjustment the object-glass is first soldered by its screw mounting to a length of brass tube which fits inside the stronger tube very well. The outer tube is attached by soldering and screwing to the flange, and carries the eye-piece itself mounted in a short length of tube in which the cross wires are fixed. The eye-piece is focussed on the cross wires as usual, the object-glass is placed in position, and the outer tube is levelled by means of the riding level. The focussing is then accomplished by sliding the object-glass tube in or out, and when the desired adjustment has been obtained, the flange is unclamped and the object-glass tube sweated in position with tinman's solder, by which means it becomes rigidly attached to the outer tube. The outer lenses of the object glass are also fixed in their mountings by means of wax, but the workmanship of the cell is so good that the wax acts merely as a means of preventing the leakage of air. No doubt some change in the position of the axis of collimation occurs as the temperature rises. This will do no harm if the position of the axis of collimation can be regarded as a function of the temperature, but the chance of irregularities must be put up with so long as brass mounts are used: with platinum a greater degree of certainty is to be expected. It is fair to say, however, that we have no reason to suspect the axis of collimation of movement rather than any other part of the apparatus. When the preliminary

focussing has been accomplished, and the soldering satisfactorily finished, the microscope is again mounted and levelled, and the final adjustment made so that the lever upsets when its pointed end rises above the cross wire by one diameter of the point. It generally happens that the focus is not quite correct, but this can now be set right by means of the eye-piece. Finally the eye piece (which is waxed and otherwise fastened to a tube several inches long sliding very tightly inside the outer tube) is finally waxed air tight and firm. All the parts of the microscope are now firmly fixed to the outer tube, and the whole is correctly focussed upon the end of the lever when the latter is in position. It remains to explain how the outer tube of the microscope is prepared. It must be remembered that the outer tube carries the riding level, and that the whole theory rests upon the assumption that the axis of collimation can be brought into an invariable position with respect to the horizontal. In order to avoid spending too much time over levelling the instrument when it is in actual process of observation, it is of some assistance to have the tube of the microscope and the V-grooves of the riding level so perfect that, in ordinary phraseology, the level will reverse. The microscope tube was ground and lapped by us on one of BROWN and SHARPE's cutter grinders, which are not recommended by the makers for producing a cylindrical surface. However, by applying care and attention and rotating the tube between centres we have succeeded in making a tube so cylindrical that we are unable by any of our appliances to detect any defect of form. We have to thank the mechanical assistant of the laboratory, Mr. JAMES COOK, for making the V-grooves so perfect that the sensitive level we employ does in fact reverse when mounted on the microscope tube.

The riding level is a very substantial affair, the frame is of brass cut away as much as possible for the sake of lightness. A cross level is attached to the frame by adjusting screws. The main level is mounted in a copper tube (see p. 232).

Quartz Thread and Lever and Attachments.

This being the essential part of the instrument, requires considerable care both in its design and its manufacture. The general methods have been described by BOYS,* also THRELFALL;† but it will suffice for the present purpose to refer the reader to a book on 'Laboratory Arts,'‡ Sections 80 to 91.

We have already referred to the fact that it is necessary to attend to the dimensions of the thread employed, and will not repeat ourselves except to point out that to arrive at the best relative dimensions as the result of a compromise necessarily implies an immense amount of experimenting. At one time the quartz

* 'Phil. Mag.,' June, 1887, p. 489. 'Journal of the Society of Arts,' 1889. 'Journal of the Physical Society,' 1894. 'Phil. Mag.,' 1894, vol. 37, p. 463.

† 'Phil. Mag.,' July, 1890.

‡ THRELFALL, Macmillan, 1898.

behaved so badly that we actually took the trouble to assure ourselves by trial of its superiority over other materials. We mounted a very fine steel wire, kindly sent to us by Mr. ELLERY of the Melbourne Observatory, on another balance, and observed that its rate of viscous subsidence was about a hundred times greater than we were accustomed to in the case of quartz. We repeated the experiment with a very fine platinum wire with a similar result.

It must not be supposed that all fused quartz, as derived from clear rock crystal, has the same properties. Almost every crystal examined by us contains both sodium and lithium—the latter in large spectroscopic quantity—indeed, we first noticed it from the colour it gave to the blowpipe flame. The observation of the almost universal presence of lithium in quartz was first made by TEGETMEIER,* a fact of which we were ignorant when we made the observation. There also appears to us to be a distinct though small difference in the viscosity of various samples of fused quartz, and this independently of the sodium or lithium they may contain. It has been our practice to select the most infusible quartz independently of the amount of lithium it contains, for lithium seems to be burned out by continued heating in the oxy-gas flame: whether this is really the case or whether the lithium forms a compound which does not give the flame re-action, we have not attempted to inquire. We have aimed at securing the greatest possible uniformity in the thread and a mean diameter of about $\cdot 0038$ centim. We do not pass a thread unless the diameter is uniform from end to end within the limits of observation (exceeding those of measurement), looking at samples taken from each end of the thread through a microscope magnifying 100 diameters. We have also spent a great deal of time in trying to make certain that there were no drawn-out air bubbles in the thread, and though we have succeeded in arriving at the satisfaction of both these conditions simultaneously, still our present practice is to ignore very small bubbles, and to direct our attention principally to obtaining uniformity. Since, however, we now adjust the torsion of one end of the thread only, we are inclined to think that for the future we would put up with a slight taper in the thread, provided of course that the twisting for adjustment was done from the thinner end.

The bow-and-arrow method of Mr. BOYS gives better threads for our purpose than the catapult method ('Laboratory Arts'), which does not lend itself to the production of threads of great uniformity. There may also be some difference of tempering, owing to the different rates at which the threads are pulled out and cooled in the two methods considered. A great deal of time may be spent in preparing the thread, for at present we have no method of predetermining its diameter. All that we can do is to be guided by experience, and shoot threads till one is got satisfying the conditions. The process is so uncertain that we have on occasion got a thread within a few days, and on others we have spent a fortnight over it. The thread which forms part of the instrument to which the observations refer took a fortnight's continuous

* 'Wied. Ann.,' 41, p. 19, 1890.

shooting. The best way of carrying out the examination is to draw the thread, comparing it all along its length with a bit broken from one end laid beside it under the cover slip of a microscope slide, the space between the slide and cover slip being filled with stained glycerine.

When a sufficiently perfect thread is obtained, it is silvered all over, as described in 'Laboratory Arts,' p. 222, and the ends are then coppered and soldered up to the supports. The centre of the thread is then coppered for about a centimetre of its length. The lever is adjusted in position, being held tight by a temporary clamp mounted from the back girder. It is then soldered up to the thread by tinman's solder. The excess of silver is removed with nitric acid, and the thread is well washed. It is surprising how difficult it is to do this thoroughly; we use a brush made of glass, but we are not sure that it is the best way.

Lever.

We have made levers of many metals, but at present use one of gilded brass wire of the smallest diameter we could get with our draw-plates, say .005 inch. The conditions to be satisfied are (1) magnetic indifference, (2) undeformability by the arrester, (3) lightness. At first we used to make levers of aluminium foil, shaped like a cross; we then tried soft annealed copper, in the hope of doing away with secular changes of shape, but it was not stiff enough to resist the arresting.

Adjustments of the Lever.—Having decided to use three turns in each half of the thread, it is necessary to adjust the lever so that the line joining the centre of gravity of the lever to the thread is nearly horizontal when the thread is twisted with this amount of twist.

It is shown in the part of this paper dealing with the theory of the instrument that with this twist in the thread the lever becomes unstable when the line joining its centre of gravity to the thread rises about three degrees above the horizontal. We have adjusted the lever in the present case so that it upsets when the thread is twisted by about three whole turns. The adjustment is made by weighting the lever with a small drop of fusible metal, rather larger than a pin's head.

In making a new machine we think it would be worth while to make the lever out of a thickish needle of fused quartz. We have occasionally thought that the thread was slipping in its silvering, but though there is a distinct danger of this happening, we have not had a really clear case. Some attempts to guard against the possibility of this, by grinding the thread flat on one side, failed on account of the way in which the thread was weakened.

The Spring and its Adjustments.

It is almost if not quite essential that one end of the quartz fibre shall be carried by a spring, otherwise the difficulty of manipulation becomes intolerable. It is also

clear that the spring must satisfy some peculiar conditions. The thread must be stretched by a constant, or nearly constant force, and the spring, while freely allowing this to occur, must be incapable of moving so that the point of attachment of the thread shall become displaced transversely. The spring must also be subject to so much damping that it will not vibrate during transport, otherwise the rate of subsidence of the thread may be affected and errors introduced. We have attempted to meet these conditions in the following manner. The spring, as shown in the drawings (Plate 13), consists of a pair of elliptical springs crossing each other at right angles, the point of support for the thread being at the centre of the crossing. The point to which the thread is attached is very light and might be lighter with advantage, so as to increase the effect of the damping.

There are four bars of spring steel (watch main-spring, in fact), which are attached to the plate carrying the coach springs so as to stand up perpendicular to the plate. The free ends of these springs are attached by wire links to the thread support. The object of this disposition is to damp down the free transverse vibrations of the support. For a long time this formed the complete apparatus, which will be referred to hereafter as the "rosette" spring.

In October, 1898, however, we had reason to believe that some small residual irregularities were traceable to a transverse movement of the thread attachment. We therefore put on three stays, made of very fine glass hairs, so as to hold the support to the three girders of the main framework. The stays were cemented in position by paraffin, and the wire linkages were also cemented at their points of contact by means of paraffin. This has been completely successful, as the observations will show. We are, however, of opinion that we could improve this part of the apparatus still further, for paraffin is not an ideal cement. In fastening the thread up to the support, and afterwards in stretching the thread, it is very convenient to have a slow adjustment. This is supplied by fastening the spring system on the end of a bar; the bar is passed through the end bearing and is adjusted by means of a nut working on a thread cut on the bar. The proper tension of the thread having been arrived at, the nut and bar are soldered up to the end bearing. In view of the great difficulty of preparing a good thread, it is well worth while to provide every possible convenience for adjustment, and for minimising the risk of breakage.

Thermometry.

We believe that we wasted some time in endeavouring to obtain consistent results with mercury-in-glass thermometers. We were very unwilling to adopt platinum thermometry on account of the loss of portability which is its inevitable concomitant. Through the kindness of Mr. GRIFFITHS we obtained three of TONNELOT's thermometers, which were studied very carefully by M. GUILLAUME before they were sent to Mr. GRIFFITHS. They were again studied by Mr. GRIFFITHS before they were sent

out to us, with the result that he wrote to say he believed they were the three finest thermometers ever made. We mention this to show that we really went to some trouble in the matter, and did not take to platinum thermometry until it was actually forced upon us. We desire to thank M. GUILLAUME and Mr. GRIFFITHS for the trouble they took in the matter. The reason why mercury-in-glass thermometers fail for our purpose is that they are too slow when of the necessary sensitiveness, that they do not give the mean temperature of the thread, and that the zero corrections present difficulties in field work. We are glad to acknowledge that it was M. GUILLAUME'S opinion from the first that platinum thermometry would be the most suitable for us. The instrument we at present employ is made simply according to the instructions of Mr. CALLENDER,* but we have made one or two small modifications in the resistance box which was constructed to work it. The platinum wire, of the diameter recommended by Mr. CALLENDER, is wound in a double spiral on a very thin glass tube, 1 centim. in diameter. The tube is mounted on an ebonite plug through which the leads pass, and which serves to screw it in to the inner tube of the balance. The tube is unsupported, except by the plug, and is arranged to lie parallel to the thread, and at a distance of 2 centims. more or less below it, *i.e.*, 2 centims. from thread to centre of tube.

When we first adopted the platinum thermometer we were of the opinion that the temperature of the thermometer would lag behind that of the thread, but experience has shown that the opposite is the case. When the temperature is rising to a maximum the maximum is always reached and passed some few minutes before the lever reaches its highest point.

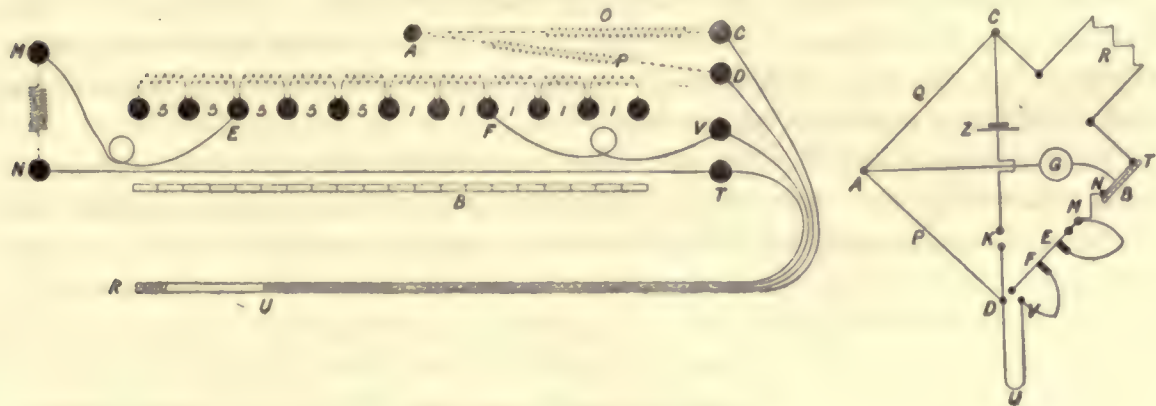
The apparent slowness of the thread in taking up the temperature of the surrounding space may be due to the following circumstance. Though we are not in possession of the complete mathematical theory of a stretched, weighted, and twisted thread, we have found by experience that an increase of tension of the thread, as by tightening the rosette spring, acts in the same way as an increase in the twist of the thread. Consequently, if the spring takes some time to reach the surrounding temperature, its effect will be the same as if the temperature of the thread itself were lagging, at all events so far as the observer at the microscope is concerned. This appears as follows. The action of a rise of temperature on the tension of the spring is complex. The expansion of the bars increases the tension on the thread; the decrease in the elastic forces of the spring produces an opposite effect. On the whole the former is probably the larger effect and therefore predominates. Consequently, the rise of temperature will stretch the thread; this will act like an increase of twist, hence less twist will be required to keep the lever in its sighted position, but this is exactly the effect produced by the temperature increase in the rigidity of the thread.

* 'Phil. Mag.,' July, 1891.

Resistance Box.

The resistance standards are made of manganin wire according to ST. LINDECK's indications.* After the box had been in use for a year it was recalibrated and found to have changed slightly, sufficiently to affect estimates of temperature supposed accurate to '002 centim. degrees. The arrangement will be seen from the diagram (fig. 2). We have five coils each of one "box unit," in our case 0.1166725 "legal

Fig. 2.



Connections of Resistance Box.

- A. The point of junction of the two equal arms P and Q.
- B. The contact of the galvanometer connection to the bridge wire.
- C. The junction of the resistance, Q, to the flexible lead of the thermometer.
- D. The junction of the resistance, P, to the flexible "dummy" lead for compensating the resistance of the thermometer leads.
- E. The connection of the short flexible lead to one end of the variable resistance.
- F. The connection of the other short flexible lead to the other end of the variable resistance.
- G. The galvanometer.
- K. The battery key.
- M. One end of the coil balancing the thermometer resistance at 5° C.
- N. The other end of the coil.
- P. One of the equal arms.
- Q. The other equal arm.
- R. The platinum wire resistance, constituting the thermometer.
- T. The junction of one of the flexible leads of the thermometer and the divided bridge wire.
- U. The end of the loop of the "dummy" lead.
- V. Junction of the "dummy" lead and the short flexible lead.
- Z. The battery.

ohm." We have also five coils five times as great, *i.e.*, equal to five box units of resistance each. The box unit is a resistance equal to the one-hundredth of the change of resistance of the platinum thermometer, when its temperature is changed from 0° C. to 100° C. The manganin bridge wire lies over a glass scale of equal parts which is graduated over a length corresponding to a resistance of one box unit. This

* 'B. A. Reports,' 1892, p. 139.

length is divided into two hundred parts, a movement of the slide over one part thus corresponding to a change of temperature of one-hundredth of a degree. Each division is 1.73 millim. long. In order to avoid the difficulty which arises from the alteration of resistance of plug contacts, we have made a slight innovation. We have placed all the coils in series, and between each of them we have brought a stout clamping terminal to the top of the box. Connection is made to the coils which it is desired to use by means of stout terminals attached to flexible leads. The diagram shows how the resistance of these leads is compensated. The "dummy" leads used to compensate the thermometer leads are made too short by the length of the flexible leads, which are, of course, made of the same wire as the dummy leads. Assuming that the temperatures of the dummy leads and of the flexible leads are the same, this gives a perfect compensation.

The advantage of choosing the particular value of the box unit above mentioned lies in the resulting fact that, setting aside corrections, the box is direct reading; the disadvantage is that with any other thermometers the box would lead to inconvenient arithmetic. The apparatus is only intended to measure temperatures between 5° C. and 35° C., consequently the large coil of the box has the same resistance as the thermometer at 5° C. The contact on the bridge wire is also of manganin, to reduce thermoelectric action, and there is no difficulty in subdividing the bridge divisions to tenths by estimation, *i.e.*, in reading to one-thousandth of a degree. We use one of AYRTON and MATHER'S D'Arsonval galvanometers and find it very sensitive and portable.

The following constants will end our discussion of this matter:—

	Legal ohms.
Resistance of platinum thermometer at 100 C.	45.99173
" " " 0° C.	34.32448
Difference	11.66725
Resistance of equal arms	10.027

Testing Resistances.

(1.) The resistance of each of the box units was ascertained in terms of the resistance of one division of the bridge wire, the wire having been previously tested for uniformity in the usual way.

(2.) The same process was gone through with the "fives."

(3.) The five box units in series were tested against each of the "fives" in succession.

(4.) The value of the large coil was ascertained in terms of the platinum thermometer at 0° C. through the intermediary of another box.

We do not desire to dwell on this part of our work, as it is foreign to the main object of this paper, but we must state that the comparisons were made with care and

repeated six times. From the comparisons a table was prepared showing the corrections to be applied at each point of the scale. The arrangement of coils adopted allows us to measure each temperature in two ways, and at every five degrees in three ways; this provides a valuable check against large errors or mistakes.

It may possibly be considered that as we have to refer to a table of corrections in any case, we wasted time in adjusting the coils with the nicety we employed. This is not the case, however, for in the process of observing it is necessary to make many approximate estimates of temperature as well as the final maximum, and the uncorrected direct readings are very useful for this purpose. We must acknowledge the assistance we received from a paper by Mr. GRIFFITHS in 'Nature,'* in which the construction of a box of coils and a standard thermometer is described.

We usually observe by closing the galvanometer circuit before we close the battery circuit. A special experiment showed that this was legitimate with our inductionless coils and thermometer, and thus we are not troubled by residual thermoelectric effects; rendered small in any case by the design of the contact maker.

The Arrestor.

The arrangement made for arresting the lever is in reality more simple than the description would seem to indicate. We have a framework adjustable to the bars of the main supports by means of clamp screws. This framework carries two jaws worked up and down by means of a pinion with teeth cut by an involute cutter. The rack teeth are therefore triangular, the tops being cut off; it is necessary to have a good smooth motion. The lower jaw of the arrestor is convex so that the lever is held against a convex surface. The upper jaw is wedge-shaped, and presses the lever against the convex surface of the lower jaw. This arrangement was adopted with a view to preventing the lever getting bent by the arrestor. The active surfaces of the jaws are connected to the racks through the intermediary of spiral springs, and the upper jaw has a stronger spring than the lower jaw. By a simple mechanical arrangement the lever is always held by the same pressural force, and this depends on the elasticity of the springs, and not on the exact angle through which the arrestor shaft may have been turned. The arrestor frame is adjusted until the lever is practically arrested in its observing position and is not displaced out of the field of view of the microscope. What happens is this. As the jaws close the upper jaw reaches a fixed position. On further turning the arrestor handle the spring of the jaw gets compressed but the jaw remains fixed. Then the lower jaw closes on the upper one, and on further turning its spring gets compressed. An essential part of this construction is that the spring of the lower jaw must be weaker than that of the upper one. The arrestor shaft of course works through a Hook's joint. Outside the thermometer end of the machine a milled head is placed, and this works a key which

* November 14, 1895.

passes through a stuffing box and fits on the end of the arrester shaft. The milled head may be clamped by a clamp screw on the end of the balance case, and thus we can make sure that the arrester does not work loose during transport. The thread being quartz in a perfectly dry atmosphere will of course insulate perfectly. We have a check on the possible electrification of the lever because we can set it swinging so as to touch the open jaws, and we can then observe whether any change in the reading occurs. We have often suspected that we were troubled by electrostatic effects but we have no conclusive evidence that this was really the case.

The whole of the inside of the balance is blacked so as to increase the surface conductivity, and so enable the temperature to equalise itself with the greatest possible facility.

In fitting the instrument together the surfaces are coated with soft wax before being screwed up. This makes all the connections air-tight. The last operation after putting the machine together is to exhaust it down to about 24 inches of mercury pressure, and then admit air dried by sulphuric acid and phosphorus pentoxide. The air is also passed over potash and through a filter of cotton wool, the object being to have dry dust-free air in the balance case.

The process of exhaustion and readmission of air is repeated many times; in making a new instrument we would have two openings into the balance and draw dry air through it instead of exhausting and readmitting air. Finally, the balance is left with air at a pressure of about 25 inches of mercury, but, of course, the actual pressure selected depends on the temperature of the balance at the time; a temperature of about 25° C. would be suitable for the pressure named. It is, of course, our object to have such a degree of exhaustion that there will always be an inward pressure wherever the balance is taken, and yet not to have a greater pressure difference than is necessary. A survey in mountainous regions would naturally require a higher degree of exhaustion.

Mounting the Riding Level.

The mounting of a sensitive bubble tube, such as is employed in our riding level, is a matter calling for attention. We have availed ourselves of the experience of our friend, Mr. G. KNIBBS, and, acting on his advice, have mounted the glass tube in a stout tube of copper, and packed it in position by means of glass wool. The packing is tight enough to put any displacement of the bubble tube out of the question, and yet the tubes are free to follow their own tendencies in the matter of expansion or contraction. We have proved by experience that a level mounted on the tube of the balance case is not sufficiently to be relied upon, and this at least suggests that some of the irregularities we have observed may be due to warping of the metal work under the influence of changes of temperature. In the event of such warping exceeding the elastic limits of the material, we should have permanent sets which

would be most noticeable after extreme temperature changes. When we come to discuss the observations we shall see that there appears to have been some effect of the kind.

Thermal Insulation.

It has already been mentioned that the copper tube, which forms the inner case of the balance, is surrounded by a packing of paper, about half-an-inch thick, over which the outer brass tube fits. It is clear that heat is able to enter or leave through the metallic ends, the sextant part being especially difficult to insulate. We, therefore, put the whole affair into a box of thin copper sheet and packed the interspace with cotton wool. It is, however, obvious that the sextant arm and the microscope must project, and, consequently, it is quite a question whether it is really worth while to insulate the other part so carefully as we have tried to do.

Packing and Transport.

The balance in its copper box is lifted by its movable handles on to a tray provided with mild steel handles, extending upwards above the top of the copper box. The tray carrying the balance is then lifted into a pine box which it just fits. Rigid connection between the machine and the box is secured by means of two hard wood strips which slip and dovetail into notches at the top of the box. When the copper box is in position the wooden strips lie exactly above it, and there are brass screws which pass from the strips into the frame of the balance inside the thin copper box, which is not strong enough in itself to form a proper connection. In this way all relative motion of the instrument and the box is avoided. The riding level is taken off the balance and screwed to the box by special screws. The pine box containing the balance is supported on a set of sofa springs, which are attached to a false bottom, and some side support is given to the box by certain iron rods which are attached to the false bottom and extend upwards, so surrounding the box by a kind of iron framework. Connection between the box and the framework is secured by means of rubber buffers, and in this way the box is prevented from swinging about on its spring bottom.

The balance is handled by means of two handles screwing into the framework through two holes in the copper lid of the outer box.

THEORY OF THE BALANCE.

The tension of the spring which stretches the thread is so large in comparison with the weight of the lever that the thread is very nearly straight; we will suppose that it is exactly so.

Let HI (fig. 1, p. 218) represent the plan of a thread lying in a horizontal plane with

a lever having mass, but of linear dimensions, fixed at the middle point of the thread. Let the thread be considered uniform in diameter, and homogeneous. Let the centre of gravity of the lever be at D, and at first consider the lever as hanging vertically, so that D is vertically below the thread. Under these circumstances, let there be no twist in either half of the thread.

Let θ be the angle through which the circle end of the thread, I, is rotated from its initial position, in other words, let θ be the twist in the circle end of the thread when the lever is kept vertical in its initial position.

Let ϕ be the corresponding quantity referring to the spring end of the thread.

Let ψ be the angle which the lever makes at any moment with the vertical plane drawn downwards through the thread.

Let l be the distance of the centre of gravity of the lever from the thread.

Let m be the mass of the lever.

Let g be the value of the earth's acceleration at the point considered.

Let τ be the moment of the forces exerted on the lever by either half of the thread when twisted through unit angle.

The equation of equilibrium, neglecting for the present the effect of variations of temperature, is

$$mgl \sin \psi = \tau (\theta - \psi) + \tau (\phi - \psi) \dots \dots \dots (1).$$

If the system is in equilibrium and we increase θ , the lever will take up a new equilibrium position, provided that $\frac{d\psi}{d\theta}$ is finite. If $\frac{d\psi}{d\theta}$ is infinite any increase of θ will make the lever upset. Now, from Equation (1) above

$$\frac{d\psi}{d\theta} = \frac{\tau}{mgl \cos \psi + 2\tau},$$

so $\frac{d\psi}{d\theta}$ will be infinite when

$$mgl \cos \psi + 2\tau = 0,$$

i.e., when

$$\cos \psi = -\frac{2\tau}{mgl}.$$

Also from the original equation

$$mgl = \frac{\tau(\theta - \psi) + \tau(\phi - \psi)}{\sin \psi},$$

so $\frac{d\psi}{d\theta}$ will be infinite when

$$\cot \psi = -\frac{2}{(\theta - \psi) + (\phi - \psi)}.$$

In the case of the instrument as constructed, we know that $(\theta - \psi)$ and $(\phi - \psi)$ are both approximately equal to 6π , so that the upsetting position of the lever is approximately given by $\cot \psi = -\frac{1}{6\pi}$, or the lever is above the horizontal plane

through the thread by about three degrees when upsetting takes place. This is in exact accordance with our observations in so far as they are able to test it, and indicates that the simplified theory is fairly applicable to the actual instrument.

The accuracy with which a setting of the microscope may be made upon the mark at the end of the lever depends upon the value of $d\psi/d\theta$, and is, therefore, greater the nearer the position of the lever at the moment of observation is to the upsetting position. When the observing position of the microscope has been chosen, ϕ and ψ become constant. In the present instrument it is found possible to observe so close to the upsetting position of the lever that the microscope can be set much closer than the circle can be read. It is because of this fact that we have adopted the plan of increasing the effective circle sensitiveness by giving the thread three whole turns. The circle has a radius of 7 inches, and with our present experience, we are inclined to think that it would be better for the future to use a larger circle and reduce the twist of the thread.

The sensitiveness of the instrument to gravitational changes is given by the value of $d\theta/dg$, and from (1) this is

$$\frac{d\theta}{dg} = \frac{ml \sin \psi}{\tau}.$$

This is greater the nearer the position of the lever chosen for observation is to the horizontal plane, in so far in accordance with the last result.

Effect of Variation of Temperature.

We find that the relation between θ and the temperature as given by our platinum thermometer scale, for the small changes in the latter factor which we encounter in practice, is a linear one, within the limits of accuracy of our observations. We may therefore include all the effects of a change of temperature in a single coefficient. Equation (1) may be written

$$\theta = \frac{mgl \sin \psi}{\tau} - (\phi - 2\psi).$$

As ϕ and ψ are independent of the temperature, and as θ decreases as the temperature rises, to make this a working formula we must re-write it thus

$$\theta = \frac{mgl \sin \psi}{\tau} (1 - \alpha t) - (\phi - 2\psi) \dots \dots \dots (2),$$

where α is the temperature coefficient and t is the platinum temperature. In consequence of the fact that the constants in this equation can only be approximately determined, we are limited to the consideration of relative values of g , so we may write the equation

$$\theta = Kg(1 + \alpha t) - C,$$

where K and C are constants.

Let θ_s be the reading corresponding to g_s the value of g at Sydney.

„ θ_m „ „ g_m „ g „ Melbourne.
 „ θ_p „ „ g_p „ g „ any other place.

We have then

$$\theta_s = Kg_s(1 - \alpha t) - C$$

with corresponding values for θ_m and θ_p .

For any one value of t we have

$$\frac{\theta_s - \theta_p}{\theta_s - \theta_m} = \frac{g_s - g_p}{g_s - g_m},$$

or

$$g_s - g_p = (g_s - g_m) \frac{\theta_s - \theta_p}{\theta_s - \theta_m}.$$

From the reading at any station at any temperature we may therefore determine the difference of g between that station and a standard station, say Sydney; provided we know the reading at Sydney at that temperature, the difference of reading between Sydney and Melbourne at that temperature and the difference in the values of g at Sydney and Melbourne.

To get an idea of the numbers involved in the use of our present instrument, we may take the Sydney reading at 21° on October 6, 1898, as 83° . We have then

Reading at Sydney 83° , corresponding to $g = 979.639$, as given by Mr. LOVE.

„ Melbourne 82° , „ $g = 979.916$, „ „

„ the Pole $70^\circ.5$, „ $g = 983.11$, EVERETT'S 'Units and Physical Constants.'

„ the Equator $88^\circ.6$, corresponding to $g = 978.1$, EVERETT'S 'Units and Physical Constants.'

The readings are those which would be given by our sextant arc, the temperature being 21° C.

From Equation (2) we get

$$\frac{\delta\theta}{\delta t} = - \frac{m\alpha \sin \psi}{\tau} g.$$

If δt is taken equal to 1° C. on our thermometric scale, we have by observation

$$\frac{\delta\theta}{\delta t} \text{ at Sydney} = - 31.50 \text{ sextant minutes.}$$

We can at once deduce that

$$\frac{\delta\theta}{\delta t} \text{ at Melbourne would be } - 31.51.$$

and

$$\text{„ „ the Pole „ } - 31.61.$$

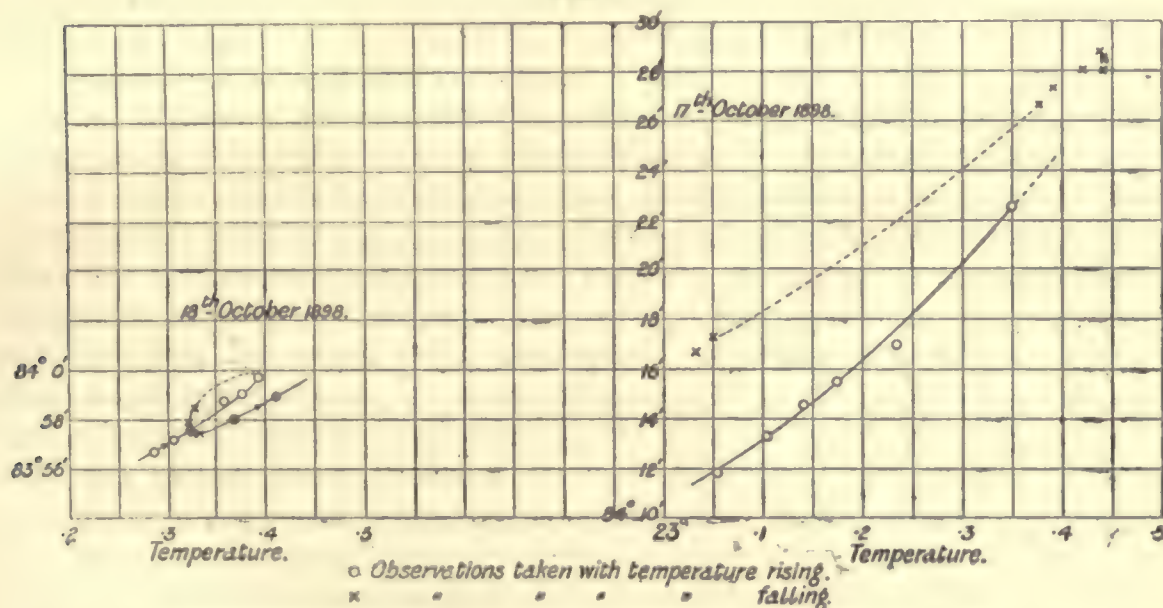
$$\text{„ „ „ Equator „ } - 31.41.$$

These values being so nearly the same, it is obvious that an approximate value of g at any station is all that is necessary to enable all observations to be reduced to a common temperature, which, if desired, may then be used to obtain a second approximation; this, however, is not necessary with our present accuracy of observation.

OBSERVATIONS.

Supposing that the line of collimation of the microscope occupies a fixed position, the variables which have to be observed at any one place are the temperature of the interior of the instrument as given by the platinum thermometer, and the amount of twist in the thread necessary at any moment to bring the image of the end of the lever coincident with a cross wire in the eye-piece of the microscope. This latter factor is given by the reading of the position of the vernier arm on the sextant arc. We have found that the relation between these variables depends very greatly not only on whether the temperature is rising or falling, and on the rate of the change, but also, theoretically at all events, on all the previous variations of temperature since the last steady state. In our instrument, the platinum wire, after a change of temperature, assumes its new resistance appropriate to the final temperature more quickly than the lever takes up its new position.

Plot 1.



In Plot 1 are given observations showing the relation between the temperature and the position of the vernier arm when the temperature is first rising and afterwards falling. The change of temperature on October 17th was due to a "southerly burster" coming up after a hot westerly wind. On the 18th the change is the

natural change which takes place every evening, the second rise of temperature being due to the room being heated by the lights used for observation. These observations gave us what we call a natural minimum. These examples are sufficient to explain the reason of our ordinary procedure which is described in the next paragraph.

Method of Observing.

In the afternoon, when the temperature of the room just commences to fall, a watch is kept by one observer on the temperature of the box. When the rise of temperature of the box becomes very slow, the other observer prepares to take observations of the lever end. The preparation consists in carefully levelling the instrument along a line parallel to the thread, placing the long striding level on the microscope, and levelling cross ways until the sum of the readings of the two ends of the bubble of this level is within a few tenths of a division of the sum found when the level was last reversed. When the observer watching the temperature considers that the temperature of the box will reach its maximum value within the next few minutes, the lever is unarrested, a note being generally made of the time at which this is done.

A careful watch being kept on the levels, the image of the end of the lever is taken slightly above the cross wire by screwing the tangent screw of the vernier arm, the motion of the screw is then reversed, and the edge of the image brought down to coincidence with the cross wire. (There is a difference in the reading of a coincidence, depending on whether the image of the lever end is brought *up* to the wire or *down* to it, of from 30" to 40" (sextant), so that settings are habitually made downwards.) An observation of temperature is taken when the coincidence is exact. Immediately a setting is made, the positions of the ends of the bubble of the microscope level are noted, and the time, temperature and level readings entered. A reading of the position of the vernier arm is then made at leisure. A complete observation takes from three to four minutes. On levelling again, if necessary, it is seen that the image of the end of the lever has moved upwards, so the former procedure is repeated, until the end of the lever remains steadily in coincidence with the cross wire. An independent entry is made in the note-book of the time at which the temperature commences to fall. The image of the lever end is watched, levelling at intervals, until it begins to come down, to ensure that the maximum reading has been obtained. The lever is now arrested, and the vernier put at the constant reading of 85° (as it happens), so that the amount of twist in the thread may be kept constant with the exception of the time, never longer than an hour, occupied in an observation. The aneroid and air thermometer readings are entered, the level reversed and then removed from the microscope, and the observation is complete.

Specimen Observation.

NATURAL Maximum. December 20th, 1898.

Time. P.M.	Temperature of instrument.	Readings of end of level.	Circle reading.	Remarks.
h. m. s.	° C.		" "	
1 1 0	21.509	Air temperature 22°.1
2 12 0	21.779	" " 22°.4
2 42 0	21.890	" " 22°.5
3 53 20	22.033	6.1 41.1	81 26 50	
3 57 30	22.033	6.2 41.1	81 26 50	
4 2 30	22.033	6.2 41.1	81 27 0	Lever continues to rise, but temperature is steady
4 21 0	22.033	6.2 41.1	81 27 20	
4 24 0	Begins to fall			
4 26 0	22.31	6.2 41.1	...	Lever turned, air tempera- ture 21°.6

Aneroid 28.2. Lever clamped at 85°			
Level reversed.	B end to eye-piece.	Readings of bubble	6.2 41.1
" "	A " "	" "	6.2 41.1
" "	B " "	" "	6.1 41.1

The time between the first indication of a fall of temperature and a fall of the image of the lever end may be anything between 0 and 12 minutes, depending on the rate at which the temperature is changing. The temperature when the image of the lever end first gave signs of coming down, has been 0.02° below its maximum value, though it is generally much less. We assume that the maximum value of the temperature corresponds to the maximum reading of the vernier arm—an assumption which can only be rigidly justified by the accordance of the results which the procedure gives. To distinguish the observation of a maximum temperature and a maximum reading when the temperature alters naturally, from readings taken in other ways, we call the former a natural maximum observation. As the hour at which the temperature rate reverses varies greatly from day to day, the preliminary watching of the temperature is rather tedious.

A minimum reading may be obtained in a similar way by waiting until both the temperature of the air and of the box are falling, the temperature of the air being lower than that of the box. This occurs, of course, every evening after sunset. It is easy now to increase the temperature of the air of the room, by using lamps or small stoves; the lights necessary for observation are generally sufficient. The temperature of the box, and the position of the vernier arm, then go through minimum values which are observed as before. A reading taken under these circumstances we call a natural minimum. The actual observing for a natural minimum does not take half-an-hour.

NATURAL Minimum. Sydney, December 18th, 1898.

Time. P.M.	Temperature of instrument.	Readings of end of level.	Circle reading.	Remarks.
h. m. s.	° C.		° ' "	
6 38 0	23.110			
7 56 0	22.950	Air temperature 22°.3, tem- perature steady
8 9 0	22.950	Temperature beginning to turn
8 12 0	22.954	6.5 41.0	81 54 30	
8 16 0	22.960	6.4 41.0	81 54 40	Independent settings (2)
8 21 0	22.969	6.3 40.9	81 54 40	
8 24 30	22.975	6.4 41.0	...	Lever "has turned"
Aneroid 28.00. Air temperature 23°.7. Lever clamped at 85° Level reversed. B end to eye-piece. Readings of bubble 6.7 41.1 " " A " " " " 6.6 41.1 " " B " " " " 6.3 40.9				

By far the greater number of our observations have been made by artificially heating the lower part of the case by placing a batwing gas burner, or a lamp, on the floor directly under the centre of the Kew magnetometer tripod, with a view of getting the temperature of the box between 2° and 3° above that of the air of the room. The source of heat is taken away after about three-quarters of an hour, and a maximum reading is obtained within the next hour. It is surprising that such barbarous treatment as heating the instrument from *below only*, with a naked flame, should have given results worth recording, but from the plots of the observations taken in this way it will be seen that they are most accordant. They will be referred to as artificial maxima. The success of this method of observing depends entirely on the perfect freedom of expansion of every part of the instrument. For reasons, which we give afterwards, we now only observe either natural maxima or minima.

ARTIFICIAL Maximum. Hornsby, December 15th, 1898.

Time. P.M.	Temperature of instrument.	Readings of end of level.	Circle reading.	Remarks.
h. m. s.	° C.		° ' "	
9 23 30	26.958			
9 30 0	27.030			
9 32 0	27.030	Temperature commencing to fall
9 34 0	27.040	6.5 40.9	84 14 0	
9 39 10	27.059	6.6 40.9	84 14 40	
9 46 30	Lever well down
Aneroid 28.20. Air temperature 24°.5. Clamped at 80° Level reversed. B end to eye-piece. Readings of bubble 6.9 41.0 " " A " " " " 6.6 40.8 " " B " " " " 6.9 41.0				

The adequacy of the temperature observation, and of the instrumental adjustments, will now be discussed.

Temperature Corrections.—Any given temperature measurement is clearly affected with the sums of the errors of the coils employed. The accuracy with which the coils are compared with each other and the bridge wire is chiefly a matter of galvanometry. We made our comparisons with the galvanometer used in the temperature observations, and, consequently, cannot hope to attain the highest possible accuracy of which the method is capable. A long series of comparisons shows that the working accuracy, or rather consistency, attained in the temperature measurements is within $0^{\circ}01$. If we suppose that any observation is in error by this amount, the resulting uncertainty may be stated as 0.3 minute (sextant). This would lead to an error in the estimation of the value of g of one part in 700,000 very nearly.

Accuracy of Setting on the Lever and Reading the Circle.—The position of the vernier arm can be read to 10 seconds of the graduation of the arc, or to 5 seconds of arc. The magnification of the microscope is such that if we move the vernier arm through 10 seconds (sextant), the end of the lever is displaced on the cross wires by a comparatively large amount—an amount two or three times larger than the least we could see. We may say then, that the accuracy of setting is such that we are not affected with any errors on this score comparable with those which occur in reading the vernier. With regard to the latter we will suppose that, taking the sensitiveness as before, an error of 10 seconds in reading the vernier arm would lead to an error in the estimation of g of one part in 1,300,000. This is about half the temperature error.

Errors of Levelling.—The indications of the instrument depend on the assumption that the line of collimation of the microscope can be brought to the same position with respect to the horizontal at each observation. We have already discussed the precautions taken to insure this being the case; but, as there pointed out, there is a certain outstanding theoretical uncertainty on this score, and, moreover, there is no way of applying a check. Setting this aside, we consider that the axis of the microscope tube occupies the same relative position with respect to the horizontal plane whenever the level reverses. The readings of the position of the ends of the bubble can be got with certainty to within 0.2 of a division. It is not always possible to adjust the level during an observation so that the bubble occupies its reversing position. In practice our observations have been made with the maximum error of 0.6 in the position of the bubble. By trial, we have found that if we displace the bubble by 9.0 divisions we alter the circle reading by 150 sextant minutes. It follows that an error of levelling of one division of the level scale would introduce an error of 0.3 sextant minute, or one part in 700,000 in the value of g .

If all these three maximum errors conspire, we shall obtain a value of g in error by one part in about 300,000. It must not be forgotten, however, that with the exception

of the temperature error, we have taken as possible errors quantities which could only be realised by bad observing and by omitting to apply a level correction, which, hitherto, we have not found requisite.

Reduction of Observations.

The readings of the instrument at any one place differ from day to day from two causes—from change of temperature and from the slow elastic after-working of the thread and its supports. When a new thread is set up, or any alteration made in the lever or supports, the first thing to be determined is the effect of temperature on the readings. When a considerable number of daily observations have been collected, in the first place, the maximum temperatures of each day's observation, as entered, are corrected according to a scheme drawn up from the comparison of the coils of the resistance box. The maximum readings of the position of the vernier arm are then all reduced to one temperature by an assumed temperature coefficient, on the assumption that the relation between the temperature and readings is a linear one. A plot is then made with time as abscissa and readings as ordinates. If there appear to be systematic errors connected with the temperature, a new coefficient is taken, and the observations again reduced. This procedure is repeated until the systematic errors cease to be apparent—sometimes a lengthy process. If there was no elastic after-working, the plot of the observations from day to day at any one place should lie on a line parallel to the axis of time. If elastic after-working exists the line joining the plots of the observations will be more or less sloped to the same axis.

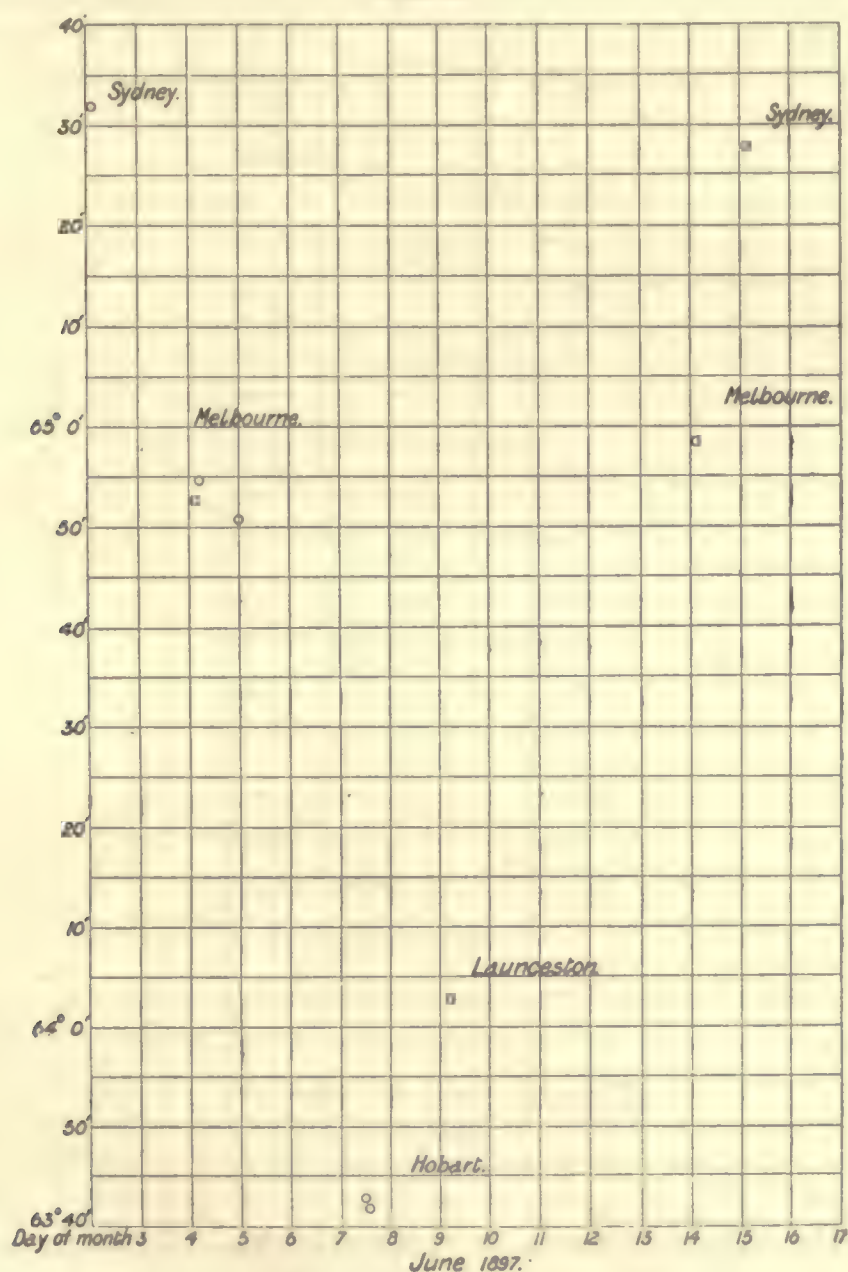
DISCUSSION OF RESULTS.

There are two conditions which a balance of this kind must fulfil for it to be a working instrument—firstly, it must give accordant readings at any one place from day to day; and secondly, the readings must not be affected by the vibration inseparable from transport. We shall adopt the historical method of treatment, discussing the deviations from the rigorous fulfilment of the two conditions in the order in which they were observed.

The first journey made with the instrument (other than preliminary ones) was commenced in June, 1897. The instrument was taken from Sydney to Melbourne by train, and set up in a cellar of the Physical Laboratory of the University. It was then taken to Hobart by steamer, observed in a cellar of the Museum and in the University Physical Laboratory, then to Launceston by train and observed in the strong room of the Custom House, then to Melbourne by steamer, and to Sydney again by train. On this trip simultaneous observations of temperature and twist were taken over long periods with the temperature rising or falling more or less rapidly, as we had not at this time discovered that it was essential only to observe

maximum or minimum readings. From the numerous observations taken we have selected those obtained under conditions most nearly approaching those which we now know to be required. They are given in Plot 2. In the long series of obser-

Plot 2.

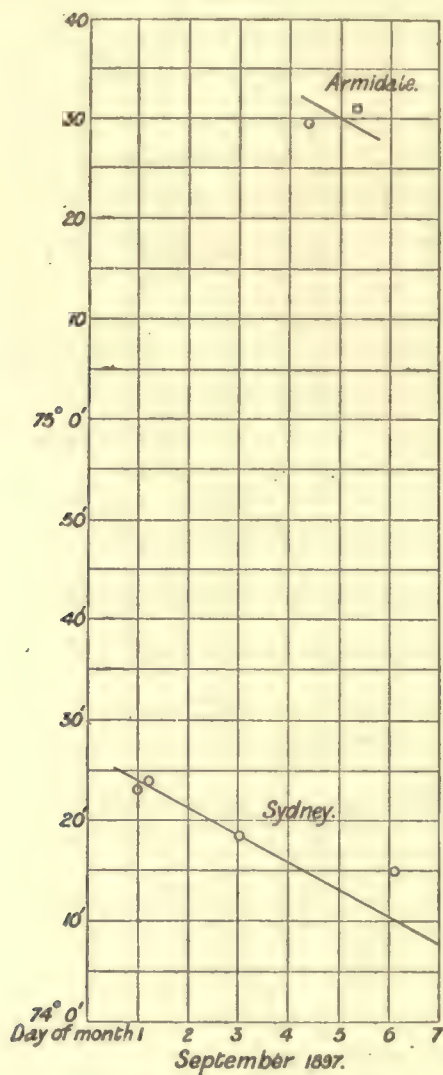


Readings reduced to 16° C.

variations taken discontinuities appeared, amounting in one instance to 7 sextant minutes. At this time the two axles to which the thread was attached were connected by a rectangular frame, intended to make both ends of the thread twist by

the same amount. This frame was put in as the result of an after-thought, after the instrument had been completed, and there was not then room for an adequately designed girder. We attributed the discontinuities observed to the bending of this frame, and it was taken out immediately on our return to Sydney, with the result that there has not been any appreciable discontinuity in a series of readings since

Plot 3.



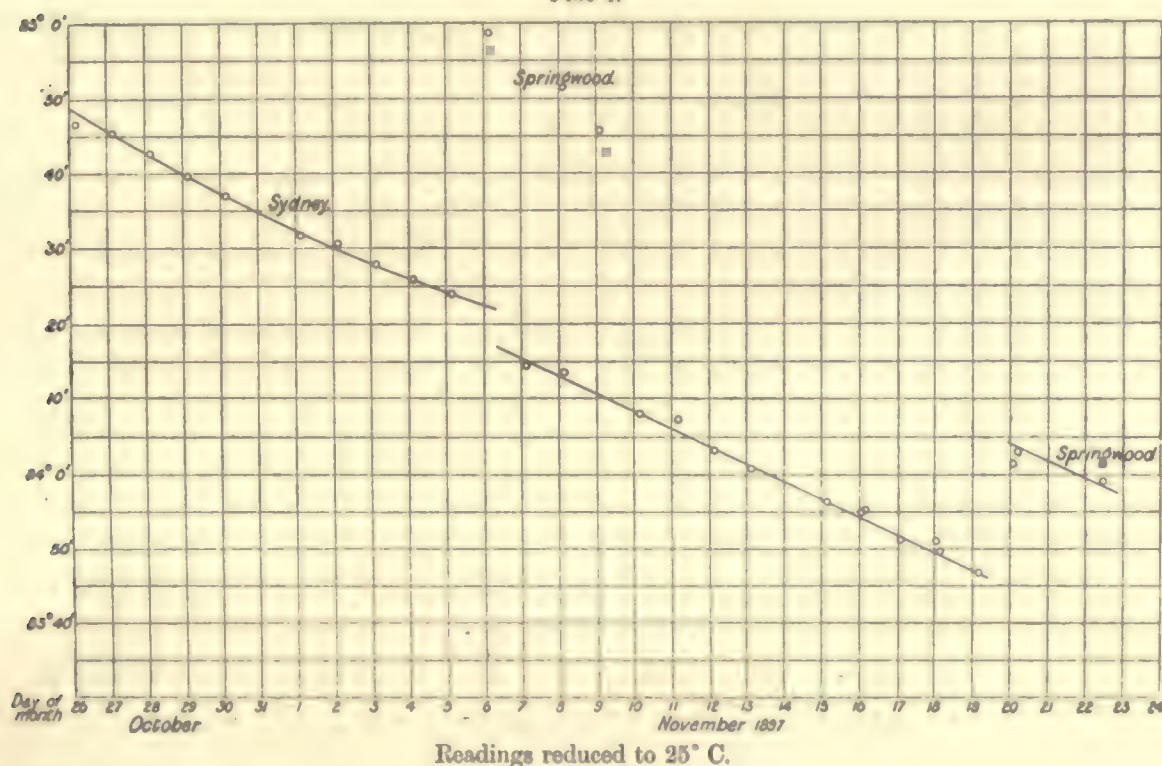
Readings reduced to 14° C.

that date. The difference between the reading at Sydney on June 2nd, and that at Melbourne on the 4th and 5th, may be taken at 39 (sextant minutes), and that between the observation at Melbourne on June 14th, and that at Sydney on the following day, as 29 (sextant minutes). The mean of these, 34 (sextant minutes), confirms, so far as it can be said to confirm anything, a result which we obtained in the following year, as will be seen later. We had quite concluded before we returned

to Sydney that the observations would not be of high value, but they afforded us some evidence that the instrument could be transported under actual conditions without serious derangement.

The removal of the frame connecting the two axles leaves one-half of the thread with a constant twist, while the other half has during each observation a slightly variable amount of twist depending on the temperature and the intensity of the gravitational force. Any change of gravitational force has now to be compensated by a change in the twist of one-half of the thread, consequently the vernier arm has

Plot 4.



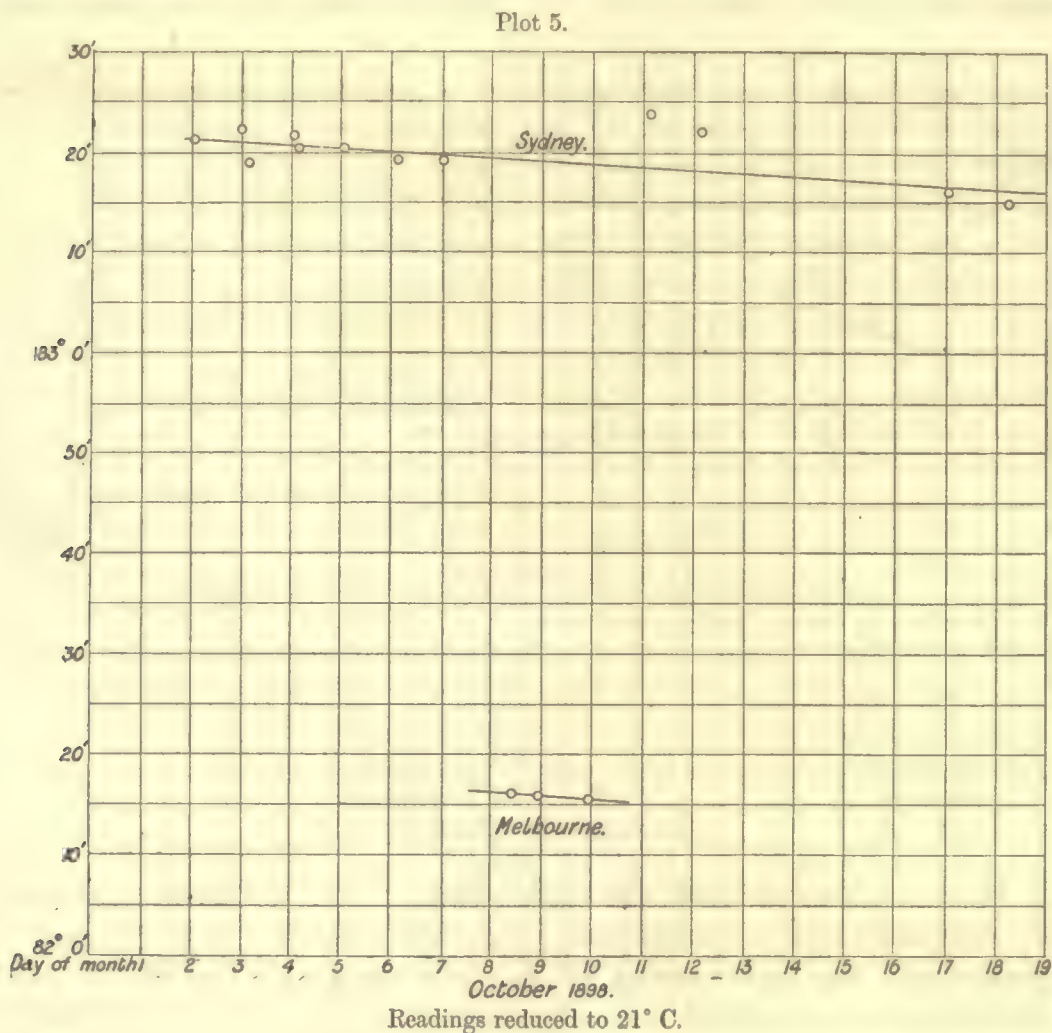
now to be moved through twice the angle necessary with the former arrangement; the reading-sensitiveness of the instrument was, in fact, doubled by this change.

A gravitational survey, connecting the towns of the eastern Queensland seaboard with Sydney, was now projected, the first connecting station chosen being Armidale, a town on the table-land in the northern part of New South Wales. The observations given in Plot 3 show an immense improvement in the behaviour of the balance, though they give evidence of a break of 5 sextant minutes in the reading on returning to Sydney—due to the shaking which the instrument had experienced in transport. We had, by this time, found out the necessity of observing only when the temperature was at a maximum or a minimum.

On the return from Armidale it was found that some air had leaked into the instrument. In trying to discover the leak, through carelessness, the delicate

soldering of the lever to the thread was severely strained. The accident had the effect of permanently increasing the reading by 10° .

On November 6th the instrument was taken by train to Springwood, a station 48 miles west of Sydney, 1216 feet above sea level. It was here observed in the cellar of the Oriental Hotel, and was brought back to Sydney the same night. Plot 4 shows that a break of 5.0 sextant minutes had occurred in the Sydney reading, and that the daily rate due to elastic after-working (about 2.5 sextant minutes per day)



had slightly increased. The balance was again taken to Springwood. On its return the next day there was no definite evidence of a further break. But a third journey on November 20th, returning to Sydney on the 23rd, strengthened the evidence as to a permanent change taking place due to the travelling. When putting the instrument into the train at Springwood on the 23rd, one of the handles of the box broke, and one end of the box fell about two feet on the asphalte. The thread was not broken, but the observation of the 23rd at Sydney differed by 1° (sextant) from

its reading on the 19th. It was considered that the breaks in the readings when the instrument was "travelled" were due to a looseness in the joint fixing the lever to the thread, which might have been caused by the accident after coming from Armidale, and observations were discontinued until the joint could be re-made.

In February, 1898, the bars carrying the thread were taken out of the outer case and the lever was re-soldered to the thread. This necessitated the little lump of fusible metal at the end of the lever being altered in order to keep the twist in the thread the same as before. In putting the instrument together again the further end of the internal framework was wedged to the copper tube. Previously permanency of relative position between the microscope and the thread depended on the attachment of the inner framework to the copper tube by the screws at the circle end only.

Other work did not permit observations to be commenced until the end of September. The temperature coefficient was now 26·7 sextant minutes per degree centigrade. Plot 5 shows that the daily rate due to elastic after-working had decreased from 2·5 minutes in September, 1897, to 0·3 minute in September, 1898. (The present thread was mounted in September, 1896.) Satisfactory observations were made in Melbourne on October 8th, 9th, and 10th. The observations on our return to Sydney show a difference of 5·5 minutes compared to the ones taken before going to Melbourne, but the change, instead of being permanent as it was in 1897, completely came out by the 17th.

The journey to Melbourne was undertaken with a view to finding the sensitiveness of the instrument. The rate, as given by the observations at Melbourne, which were completely satisfactory, is the same as that at Sydney. We may suppose it likely then that the change in the Sydney reading is due to something which occurred on the return journey. The difference between the readings at Sydney and at Melbourne, taken from the plot, is 63 sextant minutes.

If three whole turns in the thread, or 2160 (sextant degrees), are required to keep the lever horizontal against a g of 980, assuming that the relation between the necessary twist and g is a linear one, in spite of the accumulated after-working, 72 sextant minutes would be required to compensate for a change of g of 0·277, which is the difference between g at Melbourne and Sydney, as given by Mr. LOVE.*

We have then for the difference of reading between Sydney and Melbourne for the instrument, as at present constructed, calculated from the number of twists in the thread, known only approximately, 72 sextant minutes.

* Mr. E. F. J. LOVE, who has given attention to the determination of gravity at Sydney and Melbourne, both experimentally and by discussing the results by other observers, was good enough to give us the following values of g as the most probable:—

Values of gravity at Melbourne Observatory	979·916
Values of gravity at Sydney Observatory	979·639
Difference	0·277

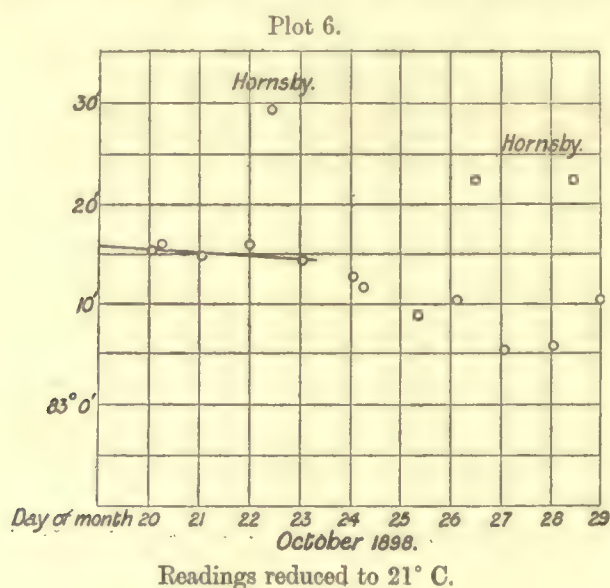
From the unsatisfactory comparison in June, 1897, remembering that the sensitiveness is doubled since that date, 68 sextant minutes.

From the comparison in October, 1898, 63 sextant minutes.

Until the difference has been more accurately determined, we may take say 60 sextant minutes as the difference of readings at Sydney and at Melbourne.

Mr. LOVE considers that the value of g at Melbourne is 979.916, and that the Sydney-Melbourne difference is 0.277. If the change in the reading of our instrument between Sydney and Melbourne is 60 sextant minutes, then a change in the value of g of 1 part in 100,000 would be represented by a change of reading of 2.12 sextant minutes.

There is now ample evidence before the reader in the plots of the observations taken in November, 1897, and from the 2nd to the 18th October, 1898, to show



that, apart from discontinuities due to travelling, it is extremely unlikely that any single observation would differ from the mean reading at any one station by 1 sextant minute.

There is only one observation, that on the afternoon of October 3rd, 1898, which differs from the mean Sydney reading by 2 sextant minutes. If, therefore, the instrument can be carried from place to place without altering its behaviour, we may say that the value of g at any station may be determined relatively to that at some standard station by a single observation, with extreme probability to 1 part in 200,000, and with certainty to 1 part in 100,000.

We had, therefore, at this time to determine the cause of the effect produced by travelling the instrument. We determined to take the balance to Hornsby Junction, a station 21 miles north of Sydney, 592 feet above sea level.

The observations at Hornsby were made at night in the lamp room of the station,

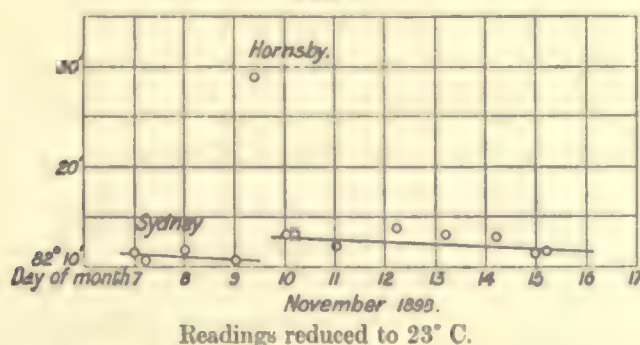
and the balance was brought back to the laboratory in the morning. The result of the observations is shown in Plot 6. Without correcting for daily rate, the Sydney-Hornsby differences of reading, as determined from these observations, are 13.5, 15.0, 12.0, 16.9, 16.4, 12.0 sextant minutes, and confirm the existence of a serious change produced by travelling. We now know that the difference is 18.2, so that from one of these observations the difference might be in error by 6.2 sextant minutes.

The only points of the instrument which we could think of as being affected by the travelling, were: the end of the rosette spring to which one end of the thread is attached, and the lever itself, the after-end only of which is clamped, leaving the forward-end not incapable of vibration. Although the end of the rosette spring was stayed by wires to four upright pieces of watch spring, it was still capable of some vibration in a direction at right angles to the length of the thread.

On October 29th, 1898, the inner framework was taken out. The arrester springs were strengthened, so that the lever was held more firmly than before. The junctions of the little wire stays of the rosette spring were paraffined at both ends to prevent the slightest play in the links, and three fine glass hairs were attached with paraffin, one end in the centre of the rosette spring and the other on one of the bars of the framework, the three glass hairs lying in a plane at right angles to the line of the thread. The point of the rosette spring may now be considered to have no freedom of movement in a direction at right angles to the length of the thread.

The instrument was re-mounted, and observations commenced on November 7th. It was found that the temperature coefficient had increased, an increase being what one would expect if the resilience of the spring system had increased, as it must have done owing to the additional constraint imposed by the three glass hairs.

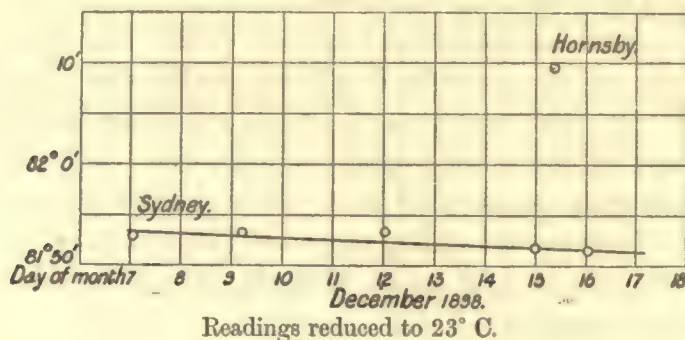
Plot 7.



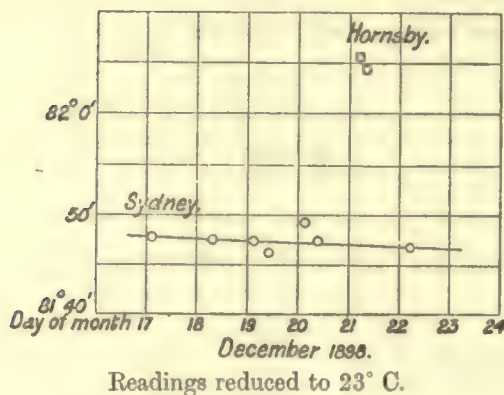
It was very soon seen that the changes due to travelling had been greatly diminished, the change in the Sydney reading, after an observation at Hornsby on November 9th, being only 2.6 sextant minutes. It was found, however, that by daily observation at Sydney, from November 10th to December 7th (those up to November 15th being shown in Plot 7), that discrepancies amounting to 4 sextant minutes on each side of the mean line now appeared in a most erratic way. This we

traced to the method of observing by heating the instrument from below with a naked flame, as before described. When we observed only natural maxima and minima, the readings at Sydney regained their old regularity, with the exception of one observation on the afternoon of December 20th, which is 2 sextant minutes from the mean line. In our present instrument there is a fault in design, inasmuch as the microscope is fixed to a copper tube, while the thread is carried by a gun-metal framework which we now try to fix firmly at both ends to the copper tube. It is only to be expected that, owing to the different expansibilities of the two metals, the instrument may be twisted in a most erratic way during changes of temperature, and this effect will be exaggerated if the changes of temperature are rapid. Moreover, by the addition of glass tie bars the character of the spring system has been entirely changed.

Plot 8.



Plot 9.



Two more journeys were made to Hornsby, and the observations are shown in Plots 8 and 9. It is seen from these plots that the readings are not now affected by travelling, for, without correcting for daily rate, we have the following differences between an observation at Hornsby and the observation before and after at Sydney :—

November 9th	18·3 sextant minutes.	
„ 10th	15·9 „ „	
December 15th	17·9 „ „	
„ 16th	18·3 „ „	
„ 20th	17·7 „ „	} Taking the mean Hornsby reading.
„ 22nd	18·3 „ „	

We may reject the observation of November 10th. Discrepancies twice as great as this from the mean were discovered afterwards to be due to observing immediately after too rapid temperature changes.

When we correct for daily rate and take the mean reading at Sydney, the Sydney-Hornsby difference comes out—

November 9th	18·5 sextant minutes.
December 15th	18·1 „ „
„ 21st	18·1 „ „

We have, therefore, determined the value of g at Hornsby relatively to that at Sydney in three journeys, with a maximum difference of 0·4 sextant minute, or to less than 1 part in 500,000 in the value of g .

This sensitiveness refers, of course, only to the Sydney-Hornsby difference. For the purposes of a survey the mean reading at the standard station may be determined with extreme accuracy—with an error at any rate negligible with respect to the probable error of a single observation at any one station. Travelling does not now affect the instrument, so that the accuracy of a determination of g , from a single observation at any station, depends on the possible deviation of a single observation from the mean.

APPENDIX B.

NOTES ON EXPERIMENTS MADE WITH VARIOUS FORMS OF GRAVITY BALANCES.

In September, 1888, we made calculations as to the sensitiveness of a balance with a horizontal thread twisted several times. We then constructed several trial instruments, mounting our threads and appliances on an old watchmaker's lathe-bed. One end of the thread was fastened to a rod working in a barrel against a spiral spring, and the other end was attached to the centre of a bar provided with a large roughly-divided circle.

A large number of trials were made as to the right thickness of the thread, &c., and much trouble was experienced in preventing the thread from breaking after having been exposed to twist and tension during several days. The thread and levers were massive compared with those we now employ. One of the earliest methods of cementing employed by us was by means of clean fusible metal. Attempts were also made to grind the thread slightly flat so as to give a sort of key to the cement.

We then began to attempt to compensate the natural increase in stiffness which occurs as the temperature of a quartz thread rises. It was clear that compensation to the requisite extent could only be attained by the use of some form of compound lever. Professor GURNEY suggested to us to try a lever consisting of three bars. Two of these were to be horizontal and situated at a short distance one above the other in the same vertical plane, they were to be of metals of as dissimilar expansibilities as possible, the less expansible one being uppermost. One end of each lever was to be attached rigidly to a cross piece to which the thread could be fastened. At the free ends of the levers the following disposition was to be made: a bar was to be pivoted from the end of the lever of the less expansible metal, and was to bear against the wedge-shaped end of the lever made from the more expansible metal. When the system of two bars was horizontal, the pivoted bar was vertical. As the temperature rose the more expansible bar would deflect the pivoted bar, and so increase the moment round the thread. Many levers were made on this principle, for which purpose we instructed ourselves in the art of the watchmaker, and finally managed to make very small levers, using aluminium and platinum-iridium as the two dissimilar metals. We finally made a compound lever weighing less than a decigram, and having all its dimensions correct to produce the compensation required. After some experimenting with this lever, it was abandoned on account of the inevitable want of permanency of form to which its hinged joint gave rise.

During the experiments with compound levers an iron box was made which would contain the whole appliance, and which was air-tight and could be exhausted. Most of our earlier trials were made in this box; it lent itself especially to the investigation of the flotation of the levers by air of different densities. We had hoped to be able to deduce the sensitiveness from the flotation effects, but the cement of uncertain density occupied so large a relative volume in comparison with the lever that these attempts failed.

By May, 1891, we had sufficient experience to hope to detect the lunar disturbance of gravity. At this time we used a lever of aluminium shaped like a cross, the thread being cemented across the shorter arm by shellac. A mirror was mounted on the lever so as to be vertical when the lever was horizontal; the mirror was close to the thread, being carried by the head of the cross. The balance, in the air-tight box, was placed in a cellar and supported on a very heavy stand, made by filling a large iron cylinder (a mine case for 500 lbs. of guncotton) with sand and stones. The temperature was taken by means of a very fine mercury in glass thermometer, the bulb of which was placed inside the iron box. The temperature of the cellar was very uniform, but was disturbed considerably by the presence of the observer. The sensitiveness of the instrument was ascertained by weighting the lever with shreds of fine wire; the calculation involved a knowledge of the distance of the shred of wire from the thread, a quantity which could not be got with any great accuracy.

The highest sensitiveness attained was that we got an observable deflection

corresponding to an increase of gravity by 7×10^{-6} of itself. This involved reading to one-tenth of a millimetre on a scale distant 3 metres from the mirror $\equiv 3$ seconds of arc. The observations, of course, included a study of the daily rate of the system, as well as of its temperature coefficient. We varied the form of the lever, the dimensions and twist of the thread, &c. Exceedingly good mirrors were made and mounted during this work, and we found that the best cementing material for thin mirrors is a mixture of equal parts of white and red lead made into a paste with a little boiled linseed oil. The mirrors were fastened on with a trace of this cement; they were left for about a day, and then stoved at 100° C. till hard. Every kind of cement deforms thin mirrors, but this paint deforms them less than anything else we tried. A variation was attempted on the following lines. Two threads were mounted, one many times the diameter of the other, the thicker one supports the working lever, the other acting as a torsionless axle. From the end of the working lever, distant, perhaps, 2 centims. from the thread, the finest possible thread also of quartz was stretched to join the second lever mounted on the thin thread, and was cemented to it quite close up to the thread. The second lever carried the mirror, and any motion of the first lever was magnified in the ratio of the distances of attachment of the connecting thread from the two main threads. We only got one-tenth the sensitiveness of our best single system by this arrangement, which was besides very cumbersome and difficult to set up. The finest quartz thread is too stiff to act properly as a flexible connection and acts more like a rigid bar.

During the latter part of 1891 we made an adjustable system of MICHELSON'S arrangement of interference mirrors, and tried to increase the sensitiveness of our angular measurements by observing the motion of the interference fringes. The general result arrived at after much patient work was that the method presented no advantages in practice; and this even when we replaced our single mirror by two small mirrors separated as far as the mechanical conditions permitted.

By March, 1892, we became convinced that it was hopeless to attempt to disentangle the lunar effect from the instrumental irregularities, even if we could bring the sensitiveness up to the necessary point; of which there seemed to be no hope. The research was therefore abandoned.

Investigations with the view of constructing our present form of portable instrument were begun in May, 1892. For this purpose we mounted a thread on the spiral head of our milling machine, and supported the fixed end of the thread on the back centre. The twisting of the thread was observed by a mirror and scale, the mirror being connected to the rod carrying the end of the thread to be twisted; and a lever and mirror were mounted at the centre of the thread as before. The machine was provided with a special slow motion of rotation for the spiral head. The position of the lever was observed by a telescope, using the method of reflected images. These trials led to the present form of balance, the construction of which was commenced in August, 1892. The instrument was not ready till July, 1893, and the

first thread was not mounted till September, 1893. This was a catapult thread, and was twisted with $2\frac{3}{4}$ turns. The aluminium lever carried a mirror, and this was observed by reflexion of cross wires as before. At first the thread was intended to be twisted from one end only to compensate changes of gravity—exactly as in our present form of instrument—but as irregularities occurred we were led to put in an extra set of bars so as to twist both ends of the thread at once. We had also an idea that the theory would be sufficiently simplified to enable us to avoid the necessity for any calibration, the total twist being capable of exact estimation in consequence of the presence of a theodolite circle, which at that time occupied the place since taken by the sextant arc. We also hoped that an exactly symmetrical distribution of twist in the thread would reduce the viscous yielding, and so more than compensate for the loss of sensitiveness due to twisting two ends of the thread instead of one.

The lever was adjusted by drops of paraffin, which are easier to regulate than drops of solder. The whole structure of the instrument was mounted on a turntable so as to allow us to take observations in any azimuth, for the purpose of eliminating magnetic effects if such should appear. In October, 1893, this machine was taken to Armidale, with the result mentioned at the commencement of the paper. The temperature was taken at this time by a mercury-in-glass thermometer.

During the time that the instrument was undergoing repair and alteration, in accordance with the experience obtained, we constructed a fresh instrument in which the whole of the working parts were immersed in mineral sperm oil. The machine was only intended as a trial instrument, and was put together out of brass tube, &c., but it was well made. We observed it in the cellar with the appliances formerly used in the attempt to discover the lunar disturbance of gravity. It was found that the readings went through a regular daily cycle which was ultimately traced down to the action of minute convection currents. The regularity of these minute currents was one of the most surprising things we have ever met with. In order to get an idea as to whether it would be possible to observe at sea, we mounted the machine on a swing, and satisfied ourselves that no amount of damping would enable accurate observations to be made under such circumstances. A subsidiary set of experiments were made in connection with this matter in order to find the resisting properties of different cements when immersed in oils, *i.e.*, to find out whether they were gradually softened by the oils. These experiments lasted for two years, and showed us that the resistance of shellac is surprisingly great. Mineral oils did not appear to have any influence at all, and turpenes only a very slight effect, the other cements tried were not nearly so resisting.

Experiments of one sort or another with the oil balance were continued till January, 1894.

Meanwhile the portable instrument had been restored, and in November, 1893, the catapult thread was replaced by a shot thread, this was under observation during the

beginning of 1894. We now had a balance much worse than the one that had been broken: the thread appearing to show a viscous yielding in the wrong direction. We attributed this to the shellac, so in January, 1894, an experimental thread was mounted on yet another balance. This thread was drawn down so as to be thick in the middle and at both ends, with the view of reducing the stress intensities in the shellac. The results of this experiment were such as to lead us to think the abnormal behaviour of the portable balance was to be traced to the thread or lever, and not to the shellac. However, by February the balance seemed to have settled down, and it was again taken to Armidale. On this occasion, however, the results were quite disappointing, and the cross wire images were so difficult to observe that it was clear that a new mirror or method of observing was necessary. The viscous subsidence from whatever cause arising was also unsatisfactory, so that we decided to mount a fresh thread, choosing now a much finer one. For two months of incessant work we struggled with fine threads, finally mounting what we thought a very good one in April, and this was then observed till July, when we have the following note: "This thread, the very finest we have had with a very small lever, has been most unreliable. It seems from its behaviour (especially when the lever becomes unstable) that the centre of gravity of the lever has been moving relatively to the thread, perhaps the fine thread has been moving through the shellac."* A defect in the arrester rendered this possible.

In consequence of this observation a separate experiment on another balance was made from May till September, using a soldered thread. We were led by this experiment to solder up a fine thread to the portable balance and to mount on it a soft copper lever. On August 21st, after continued observation, we were forced to the following conclusion:—"From the general appearance of the observations it is clear that the readings are becoming less with lapse of time—or the thread requires more twist to bring the lever to its sighted position—the effect to be anticipated . . . The readings are, however, irregular . . . The thread is not to be compared with others we have had whose variations were within a degree, whereas this thread has altered its reading by ten degrees. The thread is so fine that the centre of gravity of the lever must be extremely close to it, so that the very smallest change in the lever or attached mirror will greatly affect the reading. The very fine threads have not been a success." As a result of this experience we abandoned the lever and mirror in favour of a microscope, and also brought the arrester to its present form. During September and October, 1894, several threads were mounted, and these all broke before we could get a series of observations. These persistent failures led us to examine the threads more closely than we had done hitherto, both as to uniformity and freedom from air bubbles. Threads of the following diameters all broke: .00126, .0015, and

* We are now inclined to think that a good deal of the difficulty which we attributed to the imperfect elasticity of the threads was in reality due to bad means of attachment, imperfect spring, and bad temperature estimations.

·00154 inch. Also the twist was far less than our previous experiments had indicated as allowable. Thus, we thought that we ought to have been allowed to put in a twist of one turn per centimetre, and we only put in a twist of ·204 turn per centimetre. This showed that either we had got hold of a bad sample of quartz, in spite of all efforts to the contrary, or that the conditions of continuous stress obtaining in a balance affect the elastic properties in some hitherto unrecognised way.

Now the thin thread which did so badly from June till August, 1894, had a diameter of ·0004 inch or ·00102 centim. The length of all the threads was 12 inches. We concluded that the diameter of the thread should lie between ·0035 and ·001 centim., using levers of the mass hitherto employed, so as to avoid breakage on the one hand or irregularity on the other. The cause of breakage was also seen to be related to the sag produced by the use of too heavy a lever. It was at this time that we made the comparative examination of different samples of quartz referred to in the text. We did not terminate these investigations till the end of 1894, and it was not till March, 1895, that we succeeded in obtaining a thread to satisfy us. The diameter of this thread lay between ·0014 and ·0015 inch, and was made of our most infusible quartz and mounted with a very light straight wire lever. We observed this thread till September, 1895, finding, amongst other things, that the flotation correction was very small, as had been anticipated. The viscous yielding was large, and we suspected that the silvering had not been removed sufficiently close to the coppering (from fear of the nitric acid getting in and gradually loosening the thread); this was tested by a reapplication of nitric acid, and the reading promptly changed by 40° of twist.

Finding the great weight of the instrument a drawback, we re-made the base and replaced the theodolite circle at the twisting end by a sextant arc. By November we had traced such irregularity as still persisted, to the sticking of a barrel spring, which caused the tension of the thread to vary irregularly whenever the temperature changed. We therefore designed and made the "rosette" spring referred to in the text, but were so unfortunate as to break the thread in dismounting it; we spent no less than two months in getting a fresh thread to satisfy the conditions. On January 22nd, 1896, this thread was mounted, with about three whole turns at each end. It was observed continually until July 9th, when it was pleased to break. The daily rate of subsidence of this thread was 6 sextant minutes in March, and fell to 2·5 in the latter part of June. There appeared to be some effect depending on the time which elapsed between the releasing of the lever and the time at which the reading was taken. We did not find the reason of this at the time, but we now know that it was due to the heating up of the balance by the observer. However, we wasted some time over it.

A new thread was got in September, 1896, after some weeks' shooting. This thread is still in use and is the best we ever got. We had a great deal of trouble in stopping leaks in the apparatus, which was beginning to show signs of wear in

the bearings. In April, 1897, we detected a mechanical irregularity due to this wear, the axle of the sextant arm was working with too much friction ; this was remedied. During May the instrument was considered to be fit to travel, and we took it to Bowenfels, a place in the Blue Mountains, some 2000 feet above Sydney, and here we made some promising observations. We have to thank our friend, Mr. FLINT, for allowing us to use his house as an observing station, and for helping us in every way. When we came to discuss these observations, we found that it was now necessary to improve the thermometry, and we accordingly made and tested the platinum thermometer. By dint of some very continuous work we were able to get away to Melbourne in June. An account of our work from this date is contained in the paper.

DESCRIPTION OF PLATES.

PLATE 1.

N.B.—The drawing does not show the long inner tube carrying the eye-piece inside the outer microscope tube, otherwise it is a working drawing.

INDEX TO LETTERING ON THE DRAWING. HORIZONTAL SECTION.

- A. Axle carrying rosette spring. B. Axle carrying vernier arm. C. Rosette spring. D. Wire lever.
 EE. Glass tube carrying platinum wire thermometer wound in a double spiral.
 FF. Main bearings. GGG. One of the three bars holding the bearings together.
 H. Pinion of arrester working into two racks carrying the arrester jaws. I. Jaws of the arrester.
 JJJJ. Copper tube bored to fit the main bearings and rigid with respect to the inner mechanism.
 KKKK. Paper insulation round the copper tube. LLLL. Outer tube of polished brass.
 MMM. Levelling screws forming the supports of the balance on the tripod stand.
 NNNN. Ground and lapped tube carrying the microscope.
 OOO. Points at which connection is made to the thread by soldering.
 PPPP. Mercury stuffing boxes on the vernier and arrester shafts.
 QQQQ. (Also in the plan of the graduated arc.) Screws attaching the inner mechanism to the copper tube.
 RR. (Also in the plan of the graduated arc.) Part of the framework of the webbing of the sextant arc.
 SS. Cap of mercury stuffing box on vernier axle.
 T. (Also in plan.) One of the screws fastening the vernier arm to a strengthening piece screwing to the vernier axle.
 U. (Also on the plan of the graduated arc.) Clamping washer and lock nut with left-handed thread to insure rigid connection between the vernier arm and the axle.
 V. Clamp screw of arrester shaft.
 W. Slow-motion screw used in the preliminary adjustment of the tension of the thread, afterwards clamped by the clamp screw and soldered up to an invariable position with respect to the frame.
 Y. Box key on the arrester shaft. This key can be drawn out by unscrewing the stuffing box from the end of the balance case. The drawing shows the box key too large to pass through the hole, this is wrong.
 ZZZZ. Screw clamps or clips holding the balance proper to the under frame.

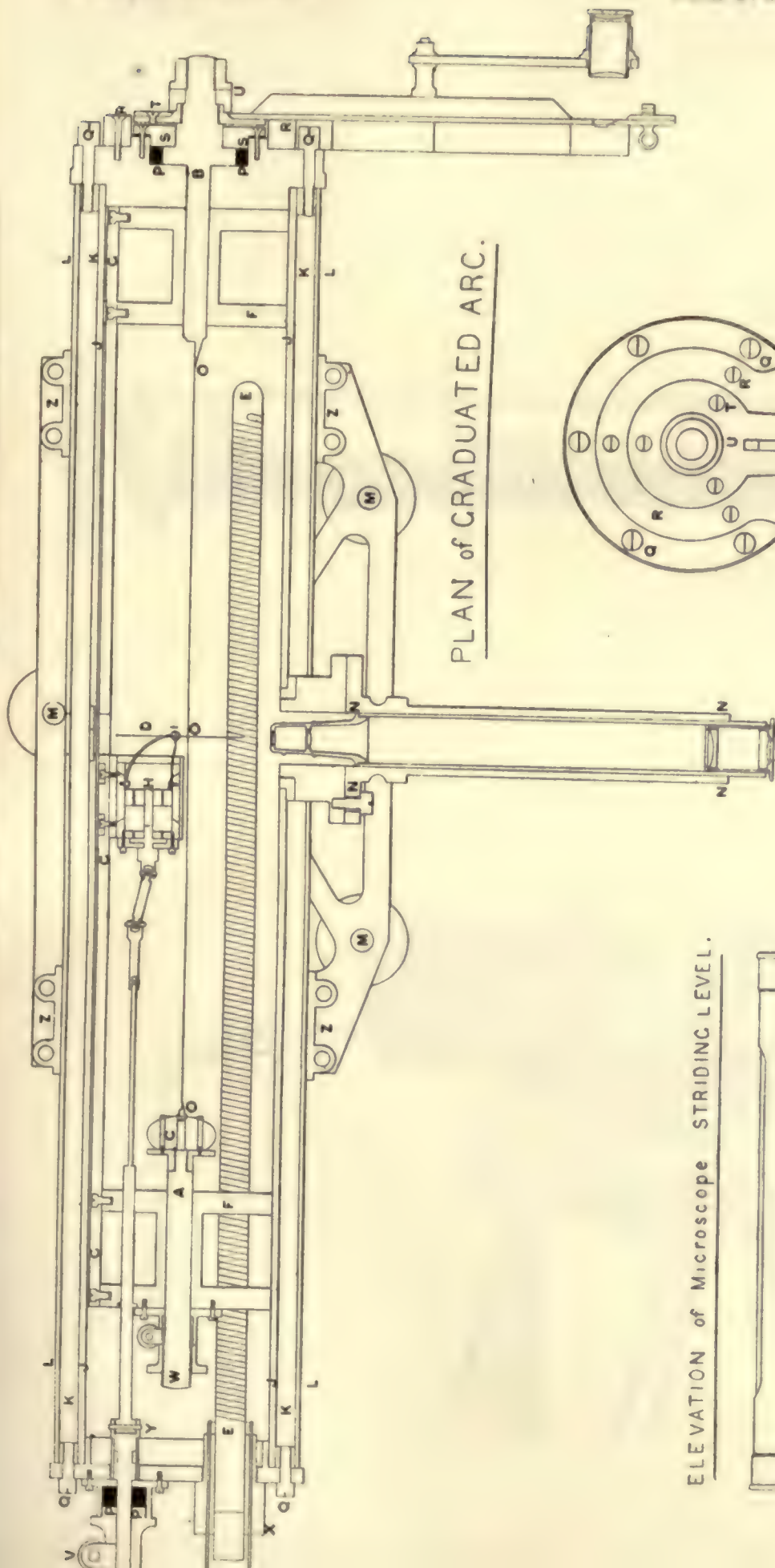
INDEX TO LETTERING OF THE ELEVATION OF THE MICROSCOPE AND STRIDING LEVEL.

- l. Level. KK. Adjustments for the level tube. C. Cross level.
 VV. The sides of the V grooves of the level carriage. MM. Worked tube carrying the microscope.

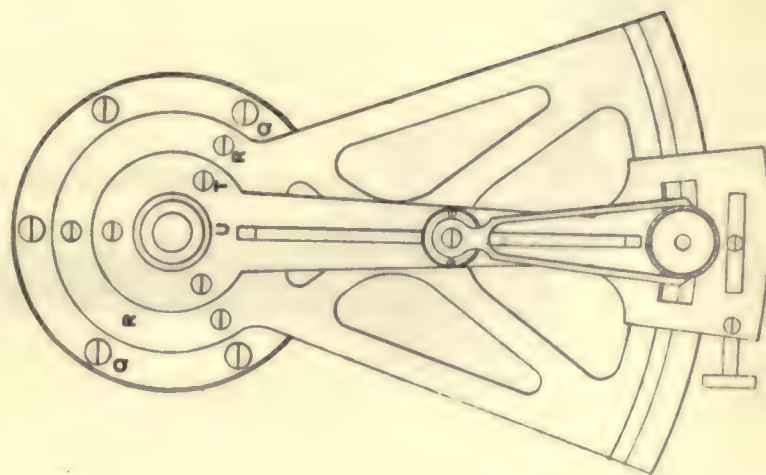
PLATE 2.

Reproduction of photographs of the apparatus.

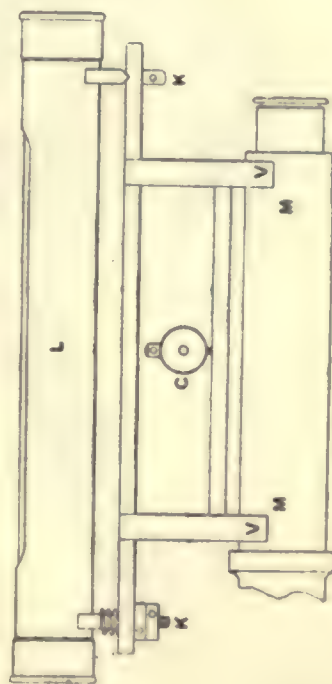
HORIZONTAL SECTION OF GRAVITY BALANCE. — $\frac{1}{5}$ SIZE



PLAN of GRADUATED ARC.



ELEVATION of Microscope STRIDING LEVEL.





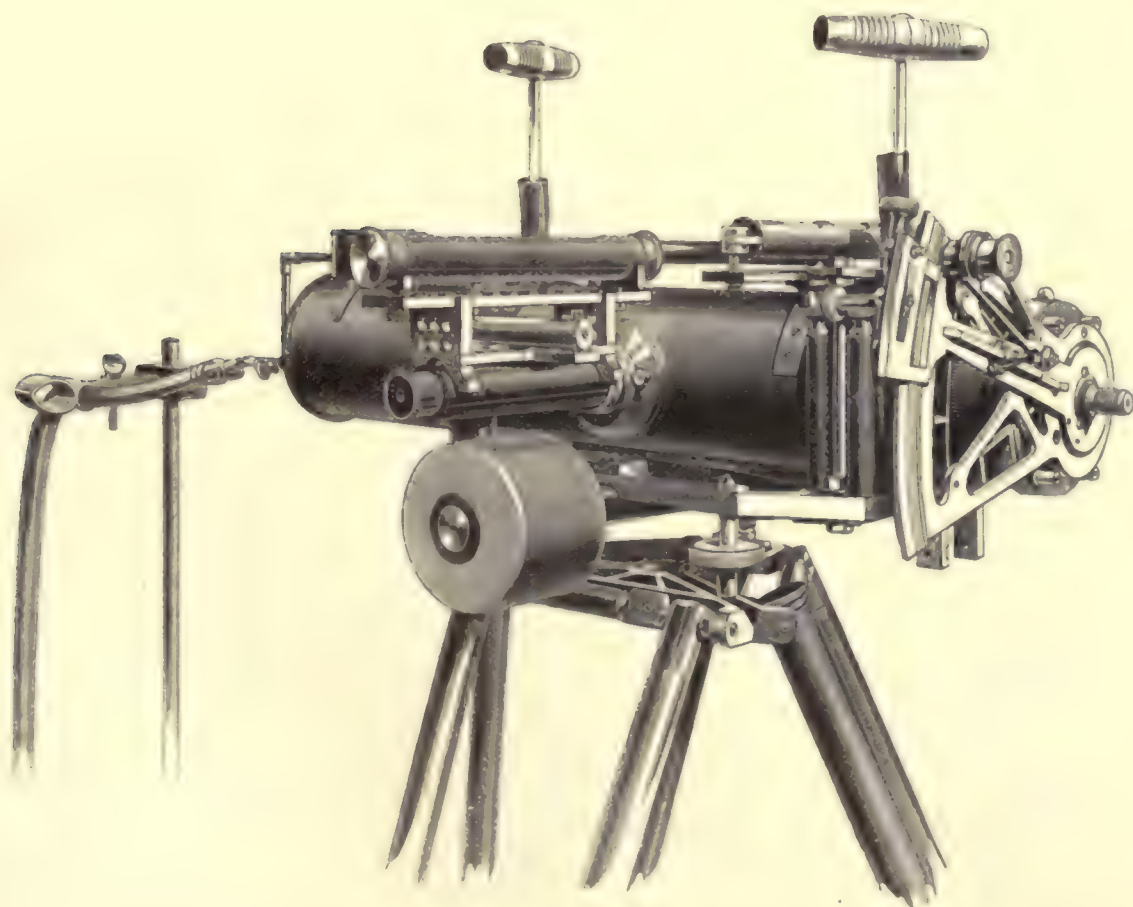


TABLE THREE

Estimated percentage of population in each age group, 1950-1959, by sex and race

Source: U.S. Census Bureau, "Age and Sex Composition of the Population, 1950-1959," Current Population Reports, Series A-1, No. 108, Washington, D.C., 1960.

VIII. *The Colour Sensations in Terms of Luminosity.**By Captain W. DE W. ABNEY, C.B., D.C.L., F.R.S.*

Received February 23,—Read June 15, 1899.

(I.) *Introductory.*

MY attention has been directed recently to the theoretical considerations involved in the production of photographs in approximately the colours of Nature, by combining together the images from three positives backed by appropriate colour screens, the colours chosen being those which should best represent the three Colour Sensations of the Young Theory.

During my investigations into the matter I found it necessary to ascertain what these colours were, for although serious objections may be raised to the Young Theory when considering it in detail, yet when expressed in a general form it adequately explains the phenomena which arise when colours fall upon the centre of the retina. The sensation curves have been given by KÖNIG, but it appeared that a redetermination by a luminosity method might well be undertaken, for they did not altogether agree with the results of some preliminary measures that I had made in order to trace them. In my work on 'Colour Vision' I have given a rough diagram as to what the sensation curves might be when they are shown as luminosities which together make up the total luminosity of the spectrum of the crater of the arc light, but it was only intended to be an approximation to the correct diagram. The method, however, by which the problem could be attacked and by which a rigid determination could be made was indicated. It is by this method that the results given in the following pages have been obtained.

(II.) *A Preliminary Survey.*

The red sensation can be perceived in purity at one end of the spectrum. From the darkest red to a point near the C line, a little above the red lithium line, the colour is the same, though, of course, the brightness varies, but the brighter red colour can be reduced to form an exact match with the dark red, and no mixture of any colours will give a red of the description we find at the end of the spectrum.

At the violet end of the spectrum we also find that the colour is the same throughout, from the extreme visible limit to a point not far removed from G, but it is not for

this reason to be accepted that the colour is due to only one sensation. It might be due to two or three sensations if they were stimulated in the same proportions along that region, and if the identical colour could be produced by the combination of other colours. Experiment shows that a combination of two colours will make violet under certain conditions, and that instead of a simple sensation of violet we have in this region a blue sensation combined with a large proportion of red sensation. The proof of this and the estimation of the percentage composition of the violet will be given subsequently. It may, however, be here stated, that if we know the percentage composition we may provisionally use this part of the spectrum as if it excited but one sensation, and subsequently convert the results obtained with it into the true sensations. Thus in calculating the percentage of red in any colour, that existing in the provisional violet sensation would have to be added to it, and the same amount be abstracted from the violet to arrive at the true blue sensation. The green sensation would remain unaltered. In the first part of this paper the provisional violet sensation will be employed and the necessary corrections subsequently made.

In using the violet it must be recollected that the colour is usually contaminated with the white light which illuminates the prism or grating, and that such illumination may be very appreciable at a part of the spectrum where the luminosity is very small. White light must therefore be cut off as far as practicable, and by use of an absorbing medium such as blue glass coated with a gelatine film dyed with a blue dye this is attained. The use of a second prism in front of the spectrum is inconvenient though effectual.

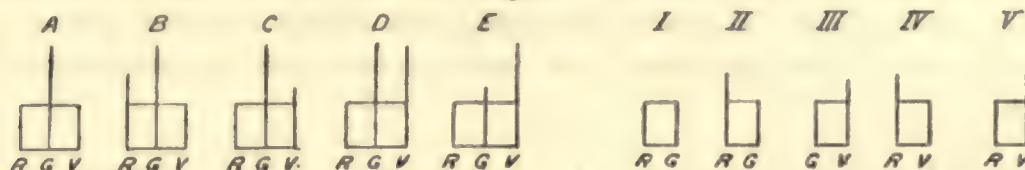
(III.) *Possible Mixtures of Sensations.*

Having at one end of the spectrum a pure red sensation, and at the other mixed sensations, due to the stimulation of the red and a blue sensation, it remains to isolate the green sensation. Owing to the overlapping of the curves in the green of the spectrum, due to the fact that this region stimulates all three of the sensations, the effect of the pure green sensation is never experienced by a normal eye, though presumably it is by what are termed the red-blind of the Young Theory. In any colour where the stimulation of all three sensations occurs, there must be always an admixture of white light, and we have to search for that point in the spectrum where white alone is added to the green sensation.

The following diagram, fig. 1, will show the variations in composition of a colour that may be met with. The provisional use of a violet sensation will not alter the argument, since, as before said, we may replace it by blue and red sensations. The different figures are purely diagrammatic. They are constructed on the supposition that equal heights of line above the base show the stimulation necessary to give the effect of white light. The scale applicable to each of the three lines is necessarily quite different to the scale of luminosity, that of the violet in particular is very greatly exaggerated. A, B, &c., mean that colours may exist each containing a

sensation of white, the amount being shown by the portions between the horizontal parallel lines. I, II, and III, &c., show colours which are due to the mixtures of two sensations. A and D are the two most interesting colours. If we take away the green sensation from A we have the mixture of red and violet which a green-blind person would match with white. Similarly, if we take away the red sensation from D we have a mixture of green and violet which the red-blind person would match with white.

Fig. 1.



The position which D occupies in the spectrum can readily be found by the normal eye, by finding that colour which, with red alone added, matches the white employed, in other words by finding the complementary colour to the red. The position of A in the spectrum is much less readily determined by the normal eye, since it requires the addition of both red and violet to make the white, a condition which is also necessary with B and C. The position can of course be determined by the aid of the green-blind eye, but a preliminary measurement of colour sensations involving the assumption of its position enables it to be fixed with the required accuracy. Before the measurements herein recorded were made such a preliminary set of observations was gone through, and the position found which was subsequently confirmed by a green-blind person. (See XXII.)

(IV.) *Precautions to be taken.*

There were several considerations that had to be taken into account in making these measures. In the first place, the white light used in the observations had to be of the same quality, that is, the relative luminosities of the different rays of the spectrum had to be constant, for it must not be supposed that the positions in the spectrum of A and D are fixed points except for the same quality of white light. They may be separated from one another by nearly the same interval in the spectrum when different qualities of white light are measured, but the larger the proportion of blue contained in the white the more they will approach the more refrangible end of the spectrum. For instance, the positions will be nearer the red with the white light emitted by the crater of the positive pole of the electric light than they would be with light of the sun on a June day near noon. Again, the final equations, for white light, given in terms of the three sensations will vary according to the white light employed, and they will also vary according to the extent of the area of the retina on which the colour images fall. This last variation is caused by the absorption by the macula lutea, and may differ in different eyes. If,

however, we can express the colours in all parts of the spectrum in *percentages* of luminosity of the three sensations, we can readily convert the equation derived for one quality into that for any other.

Bearing in mind the effect of the retinal area, it will be seen that it is necessary always to compare the patches of mixed colours when of the same size and viewed from the same distance, and with the centre of the retina. The light from the crater of the positive pole of the arc light, being always of the same quality and of great "whiteness," and giving a spectrum which is rich in blue rays, may be conveniently adopted as a standard. Moreover, this white seems to be of the same quality as the white light seen outside the colour fields, thus approaching to the fundamental white sensation.

(V.) *Method of Finding the Value of the Red and Green Sensations.*

It need only be stated that no blue sensation was found from D (sodium line) to the extreme limit of the spectrum in the red, and that in the yellow the amount found is very small compared with that of the red and green sensations. So below D to the red lithium line we have a mixture, in varying proportions, of pure red and green sensations, and from D to the yellow-green the same two sensations, but not absolutely free from the third sensation.

A colour in the spectrum which matches a solution of bichromate of potash will thus only excite the red and green sensations, and if we can find out in what proportions the two exist as luminosities in a given luminosity of the colour, we can readily determine the sensation luminosity composition of any other colours by means of ordinary colour equations expressed as comparative luminosities. To ascertain the composition of such an orange colour was the object of the first part of the investigation.

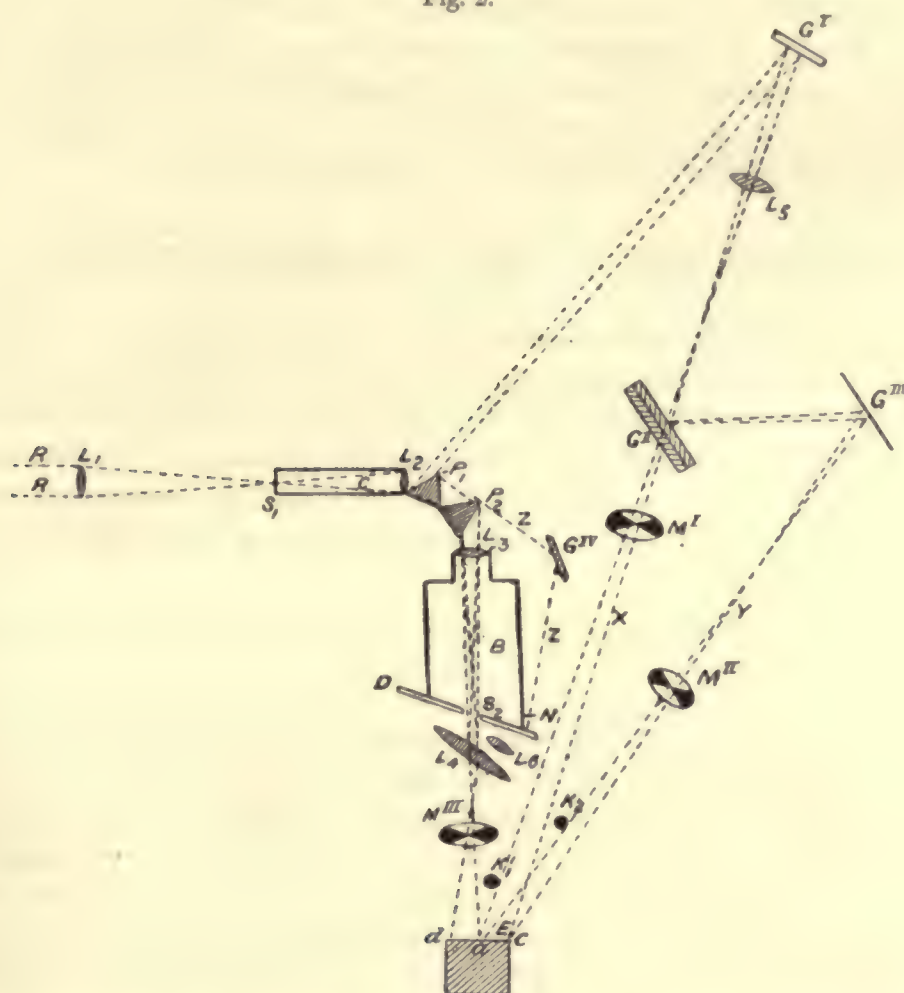
Turning to II, in fig. 1, we see that we have only to add to the colour it represents such a quantity of properly chosen violet to form white, the red and green sensations being present in the proper proportions. If, therefore, we ascertain the complementary colour to the violet, we shall find the colour which is equivalent to II, and this we find to be in the yellow. Having ascertained the luminosity of the red and green sensations in the orange, and from them the relative luminosities of the same two sensations in the complementary colour to the violet, we at once get in terms of the red, the green, and the (provisional) violet sensations the equation to the white light of the quality we may be using.

(VI.) *Apparatus Employed.*

The colour patch apparatus employed in 'Colour Photometry' was again used (fig. 2). The rays R, R, coming from the crater of the positive pole of the electric light, were collected by a lens, L₁, and an image of the crater thrown on the slit S₁.

After passing through the collimator C, the rays emerged as parallel rays; part passed through the prisms P_1 and P_2 , were collected by a lens, L_3 , and a spectrum was formed on a slide, D (which will be more fully described), in which slits could be placed, and an image of the surface of the first prism was formed on the white-red surface of a cube, E, by means of the lens L_4 , so arranged that the image of one edge of the prism fell at a , the other edge falling outside d . The other beam which passed through the collimator was reflected from the surface of the first prism to a mirror, G^I , and passed

Fig. 2.



through a lens, L_5 , then through a bundle of glass, G^{II} , placed at an angle to the beam, and on to the surface dc of the cube, a rod, K_1 , being placed in its path, to secure that this white beam did not fall on ad , on which the colour mixture fell. The portion of the beam which was reflected from G^{II} was again reflected by G^{III} , a silvered mirror, on to ac , a rod, K_2 , being placed in its path to prevent it falling on ad . In all three beams, sectors, M^I , M^{II} , and M^{III} , were placed, to allow any or all to be reduced in intensity at pleasure. In the beams X and Y any absorbing medium desired could

be placed. A small ray of light, Z, was allowed to pass beyond P_2 , and fell on a small mirror, G^{IV} , which reflected it on to the back of D, casting a shadow of a needle, N, fixed to B, the camera, on S, a scale at the back of D.

L_6 is a lens of short focus which could be moved into a fixed position behind L_4 to throw an enlarged image of the slit on a scale placed below *dc*.

In order to form colour mixtures on *ad* three slits had to be placed along the surface D. The slits were arranged in an open brass frame which slid along the plane D in grooves cut in B. At the bottom and top of the frame or slit holder two pairs of grooves were cut. In the front pair the slits could slide and be clamped in any desired position as determined by a scale engraved along the lower groove, whilst the back pair of grooves was used to hold blackened cards which filled up the intervals between the slits. The position of the slit holder was determined by the shadow cast by the needle N on the scale engraved on its back.

(VII.) *Ascertaining the Position of the Slits in the Spectrum.*

By placing one slit at some fixed number on the front scale and then causing the slit holder to move along the spectrum till known lines (due to metals vaporised in the arc) passed through the centre of the aperture, and there noting the scale number at the back, the position of the slits however placed was known. The position of the principal Fraunhofer lines in regard to the front scale was thus determined when the slit holder was placed in a fixed position as indicated by the needle shadow.

(VIII.) *Method of Determining the Colour Sensations in an Orange Ray of the Spectrum.*

It has already been stated that from a preliminary survey it was found that in the orange no blue sensation was excited, and that only red and green had to be determined. Further, it was stated that A, fig. 1, was a colour where the green sensation existed mixed only with white. If these two slits were placed in the spectrum, one in the pure red which only excited the red sensation, and the other at A, it should be possible to make such a mixture of the two colours that they should match the orange colour to which white in known quantity was added. A cell containing bichromate of potash in solution was placed in the beam X, and one slit in D (fig. 2) was caused to traverse the spectrum till the colours appeared to match. It was found, however, that the bichromate was a little paler than the orange of the spectrum, and the beam Y was diverted so that it fell only on *ad*. The white was diminished till a match was secured and the luminosities of the two were measured, when it was found that the bichromate colour contained 4.995 per cent. of white as compared with the orange that matched it.

The bichromate solution could now be used to give a colour to be matched. The

slits were placed at Slit Scale Nos. (afterwards designated as SSN) 205 and 288.5 (the latter number having been found by preliminary trials to be A), and a mixture of the two beams fell on *ad*, making as near a match as possible with the colour of the bichromate solution placed in the beam X. To the latter was added white from the beam Z, and by altering the sectors and slits a perfect match could be obtained. This being effected the width of the slits was measured by the method which has been indicated in describing the apparatus. The small lens, L_6 , was pushed in position to the centre of the lens, L_4 , and the slits successively brought into the colour which passed through the centres of these two lenses by sliding the slit holder along the spectrum. A magnified and sharp image in monochromatic light was then thrown on the scale below, *dc*, and the relative width of the apertures noted. This plan obviates recourse to wedges for measuring, and is very convenient. It has been employed by myself for measuring pin holes and other small apertures. The slits having been measured they were replaced in position, and the luminosities measured as has been described in 'Colour Photometry,' Part I.* Other matches were made and the aperture of the slit again measured, but the luminosity not necessarily, as the relation between width of slit and luminosity was determined from the first observations. Had the area of the retina on which the image fell been the same as that employed in 'Colour Photometry,' Part III.† and if the quality of the white had not been slightly changed by the interposition of the bundle of glass, G^{III} , the luminosities might have been taken from the tables in that paper.

The form of the equation then becomes of this kind—

$$m(R) + n(G) = a[(Or) + (w)] + b(W) \quad . \quad . \quad . \quad . \quad . \quad . \quad (i.),$$

where R, G, Or, W, and *w* stand for the red, the green, the orange, the added white, and the white in the bichromate solution colour respectively, and *m*, *n*, *a*, *b* constants.

Now as the orange can contain but two sensations, and as the red is a pure sensation and consequently not contaminated with white, it follows that $a(w)$ and $b(W)$ must be in nG , and we get

$$m(R) + [n(G) - a(w) - b(W)] = a(Or) \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii.).$$

That is, when the luminosity of the white is deducted from the luminosity of the green we get the green sensation left, and, finally, we get

$$m(RS) + n'(GS) = a(Or), \quad . \quad . \quad . \quad . \quad . \quad . \quad (iii.).$$

where RS and GS are the red and green sensations respectively.

* 'Phil. Trans.,' A, 1889.

† *Ibid.*, 1896.

(X.) *Method of Determining the Composition of the Rays in the Blue End of the Spectrum.*

The most ready method of determining the percentage composition of the colours which lie between *b* and the violet, is as follows : a slit is placed in position to allow a blue of a natural wave-length to pass, and a second slit is placed at the SSN which corresponds to the yellow, whose composition is already determined. No mixture of blue and this yellow will make a white corresponding to that we have to compare with it, but the slit-holder can be moved towards the red till a match is made, *i.e.*, where the slightly redder yellow is complementary to the blue which passes through the first slit. The shift of the slit-holder from the fixed point is noted, and from it are calculated the new positions of the two slits. From the previous measures made in the red orange and green portions of the spectrum, the percentage composition in red and green sensation-luminosity is known, and the luminosity of the light coming through the slit in the redder yellow is divided proportionally between these two sensations, and we have an equation of the form

$$\alpha'' (\text{RS}) + \beta'' (\text{GS}) + \gamma'' (\text{B}) = 100 (\text{W}).$$

The standard equation (vii.) is used as before, and we get the blue (B) in terms of the two sensations and the violet.

(XI.) *Method of Determining the Composition of the Violet.*

The last determination that has to be carried out is the composition of the violet. We already know that up to a point near G it is uniform in colour. But if we place a slit in the blue near the blue lithium line, and another in the red near the red lithium line, and endeavour to match the violet, we shall find that although we get a purple, yet it is too pale ; a third slit is placed in the violet, and by a right-angled prism the beam is diverted and again deflected to fall on *da*, fig. 2, and the white beam Z is also reflected to fall on the same part of the white surface. The mixture of red and blue falls on *ac*. White is added to the violet till a match is made. The luminosities of all the colours and the white are compared together, and an equation is formed of this form

$$a (\text{V}) + b (\text{W}) = m (\text{B}) + n (\text{R}).$$

Now, as the red contains no white sensation, that shown on the left-hand side of the equation must be found in the blue, a proportion of blue, green and red going to form it. All the green sensation must be "used up" in forming the white, and only the blue sensation and the red sensation can remain beyond the white. We thus get

$$\begin{aligned} a (\text{V}) &= n (\text{RS}) + [m (\text{B}) - b (\text{W})] \\ &= n (\text{RS}) + m' (\text{BS}). \end{aligned}$$

By taking colours on each side of the blue lithium line we find that the proportions of blue and red sensations are unchanged, and always fulfil the above equation.

Having found the percentage composition of all the spectrum in terms of the red and green sensations and of violet, the last is converted into blue sensation and red sensation. The red sensation existing in the violet is then added to that already found.

(XII.) *Difficulties in making the Observations.*

The description of the nature of the observations may make it appear that they are simple, but the reverse is the case. The labour involved is very great, and the difficulty soon becomes apparent when the work has fairly started. The sensitiveness of the eye to colour varies considerably, and this in itself makes observations hard. On some mornings, when coming fresh to the laboratory, the comparisons are readily made, but those made in the evenings after a day's work are often wild at first, and much more time has to be spent in perfecting them than may be supposed. Before any match can be considered worthy of recording, the eye has to be withdrawn from the light and to look into darkness for a minute at least, when a rapid glance will show if it needs alteration. If not correct, the slits have to be opened or closed, as may be required, and again a rest given to the eye. This procedure may be repeated several times before the match is considered satisfactory. The fatigue of the retina has a good deal to say to the difficulties encountered.

(XIII.) *Order of the Observations.*

It may be as well to record the order in which the observations were made. The first are preliminary, and are as follows:—

- (1.) The position of the spectrum in regard to the slit-holder is determined.
- (2.) The scales at the back and front of the slit-holder are compared.
- (3.) The lens with which the apertures of the slits are measured is adjusted.

The second are those taken for recorded observations:—

- (1.) The slits are placed in position.
- (2.) The matches are made.
- (3.) The luminosities of the light coming through the slits are measured and the apertures of the sectors noted.
- (4.) The widths of the slits are measured.

2 and 4 had to be repeated several times in each series of observations. I have already shown, in "Colour Measurement and Mixture," that a certain percentage of coloured light can be hidden in white without being perceived. In making a match with the white, each slit had to be opened in turn till it was evident that an excess

of coloured rays was issuing from it, when it was closed till the match was made. Again it was closed till it was evident that the colour was in defect, when it was opened till the match appeared correct. A mean of six observations was taken as being the most probable value of the mixture.

(XIV.) *The Red and Green Sensations Unmixed with Violet.*

To find the luminosities of the red and green sensations in the orange which matches a solution of bichromate of potash.

$$\begin{array}{ccc} W & R & 288.5 \\ \text{(Bich)} + 16.5 = & 45.5 + & 32. \end{array}$$

W

In the bichromate there is 4.5. Therefore

$$\begin{array}{ccc} W & R & 288.5 \\ \text{(Or)} + 21 = & 45.5 + & 32. \end{array}$$

$$\begin{array}{ccc} RS & & G \\ \text{(Or)} = & 45.5 + & (32 - 21) \end{array}$$

$$\begin{array}{ccc} RS & GS \\ = & 45.5 + & 11. \end{array}$$

Therefore

$$\begin{array}{ccc} RS & GS \\ (1) \quad 100 \text{ Or} = & 80.53 + & 19.47. \end{array}$$

Taking another example in detail, the slits being at 205 (R) and 270 (G),

$$\begin{array}{ccc} W & R & 270 \\ \text{(Bi)} + 8.5 = & 39.95 + & 24.5. \end{array}$$

$$\begin{array}{ccc} W & W & R & 270 \\ \text{(Or)} + 4.5 + 8.5 = & 39.95 + & 24.5. \end{array}$$

$$\begin{array}{ccc} R & 270 & W. \\ \text{(Or)} = & 39.95 + & 24.5 - 13 \end{array}$$

$$\begin{array}{ccc} R & 270' * \\ = & 39.95 + & 11.5. \end{array}$$

$$\begin{array}{ccc} R & 270' \\ (2) \quad 100 \text{ (Or)} = & 77.6 + & 22.4. \end{array}$$

* 270' means 270 deprived of all violet.

It was found in forming the equations to match white that

$$\begin{array}{cccc} W & R & 288.5 & V \\ 100 = 47.06 + 51.79 + 1.15. \end{array}$$

Also

$$\begin{array}{cccc} W & R & 270 & V \\ 100 = 39.30 + 59.15 + 1.55. \end{array}$$

From which equation we find that

$$\begin{array}{cccc} 270 & R & 288.5 - V \\ 22.4 = 2.94 + 19.46. \end{array}$$

$$\begin{array}{cccccc} R & 270 & R & R & 288.5 & V \\ 77.6 + 22.4 = 77.6 + 2.94 + 19.46. \end{array}$$

that is in (2).

Or

$$(3) \quad \begin{array}{cc} RS & GS \\ 100 (Or) = 80.54 + 19.46. \end{array}$$

Similarly it was found from slits placed at 205 and 283 that

$$(4) \quad \begin{array}{cc} RS & GS \\ 100 (Or) = 80.50 + 19.50. \end{array}$$

Other determinations gave a mean of

$$(5) \quad \begin{array}{cc} RS & GS \\ 100 (Or) = 80.50 + 19.50. \end{array}$$

The (Or) has SSN (.236), therefore

$$\begin{array}{ccc} (.236) & RS & GS \\ 100 = 80.50 + 19.50. \end{array}$$

(XV.) *Determination of the General Provisional Equation for White.*

Now the complementary colour to the violet at SSN 390 is SSN 245, and it was found that

$$\begin{array}{ccc} 236 & RS & 245 \\ 100 = 35.86 + 64.14. \end{array}$$

But

$$\begin{array}{ccc} 236 & RS & GS \\ 100 = 80.50 + 19.50. \end{array}$$

Therefore

$$(6) \quad \begin{array}{ccc} 245 & RS & GS \\ 100 = 69.60 + 30.40. \end{array}$$

Also it was found that

$$\begin{array}{ccc} W & 245 & 390 \\ 100 = 98.32 + 1.68. \end{array}$$

Therefore

$$\begin{array}{cccc} W & RS & GS & VS \\ (7) \quad 100 = 68.42 + 29.90 + 1.68, \end{array}$$

which is the equation to white in terms of RS, GS, and the provisional violet sensation.

(XVI.) *Determination of the Sensation Values in the Orange, Yellow, and Green of the Spectrum.*

The slits placed at SSNs 220, 285, and 390.

$$\begin{array}{cccc} 220 & 285 & 390 & W \\ 48.27 + 50.52 + 1.21 = 100. \end{array}$$

But as will be seen subsequently

$$\begin{array}{ccc} 285 & RS & GS & 390 \\ 100 = 42.71 + 56.37 + .92. \end{array}$$

Therefore

$$\begin{array}{cccccc} 220 & RS & GS & 390 & 390 & W \\ 48.27 + 21.577 + 28.472 + .465 + 1.21 = 100. \end{array}$$

Or

$$\begin{array}{ccc} 220 & RS & GS \\ (8) \quad 100 = 97.04 + 2.96. \end{array}$$

There is a small residuum of V equal to .01 left, but as it is non-existent at this part of the spectrum it is added to the GS.

Slits at SSNs 228, 294, and 390.

$$\begin{array}{ccc} 228 & 294 & 390 \\ 59.80 + 39.86 + .34 = 100. \end{array}$$

$$\begin{array}{ccc} 294 & RS & GS & 390 \\ 100 = 37.57 + 59.08 + 3.35. \end{array}$$

From which we get

$$\begin{array}{ccc} 228 & RS & GS \\ (9) \quad 100 = 89.37 + 10.63. \end{array}$$

The percentage composition of SSN 236 we have already found as

$$\begin{array}{ccc} 236 & RS & GS \\ 100 = 80.50 + 19.50. \end{array}$$

Slits at SSNs 240 and 205 to match 236.

$$\begin{array}{rcc} & 236 & 205 & 240 \\ \text{But} & 100 = 22\cdot24 + 77\cdot76. \end{array}$$

$$\begin{array}{rcc} & 230 & \\ \text{Therefore} & 100 = 80\cdot50 + 19\cdot50. \end{array}$$

$$\begin{array}{rcc} & 240 & \text{RS} & \text{GS} \\ (10) & 100 = 74\cdot92 + 25\cdot08. \end{array}$$

The percentage composition of 245 has already been found.

$$\begin{array}{rcc} & 245 & \text{RS} & \text{GS} \\ & 100 = 69\cdot60 + 30\cdot40. \end{array}$$

Slits placed at SSNs 205, 250 and 390.

$$\begin{array}{rcc} & \text{RS} & 250 & 390 & \text{W} \\ \text{But} & 13\cdot78 + 84\cdot56 + 1\cdot66 = 100. \end{array}$$

$$\begin{array}{rcc} & \text{RS} & \text{GS} & 390 \\ \text{Therefore} & 68\cdot42 + 29\cdot90 + 1\cdot68 = 100. \end{array}$$

$$\begin{array}{rcc} & 250 & \text{RS} & \text{GS} & \text{V} \\ (11) & 100 = 64\cdot62 + 35\cdot36 + \cdot02. \end{array}$$

In a similar way the following percentages were found.

$$\begin{array}{rcc} & 260 & \text{RS} & \text{GS} & \text{V} \\ (12) & 100 = 55\cdot68 + 44\cdot17 + \cdot15. \end{array}$$

$$\begin{array}{rcc} & 270 & \text{RS} & \text{GS} & \text{V} \\ (13) & 100 = 49\cdot23 + 50\cdot55 + \cdot22. \end{array}$$

$$\begin{array}{rcc} & 275 & \text{RS} & \text{GS} & \text{V} \\ (14) & 100 = 46\cdot75 + 52\cdot89 + \cdot36. \end{array}$$

$$\begin{array}{rcc} & 280 & \text{RS} & \text{GS} & \text{V} \\ (15) & 100 = 44\cdot77 + 54\cdot94 + \cdot54. \end{array}$$

$$\begin{array}{rcc} & 283 & \text{RS} & \text{GS} & \text{V} \\ (16) & 100 = 43\cdot63 + 55\cdot60 + \cdot77. \end{array}$$

$$\begin{array}{rcc} & 285 & \text{RS} & \text{GS} & \text{V} \\ (17) & 100 = 42\cdot71 + 56\cdot37 + \cdot92. \end{array}$$

$$\begin{array}{rcc} & 288\cdot5 & \text{RS} & \text{GS} & \text{V} \\ (18) & 100 = 41\cdot24 + 57\cdot74 + 1\cdot02. \end{array}$$

$$(19) \quad \begin{array}{cccc} & 290 & \text{RS} & \text{GS} & \text{V} \\ & 100 & = 40\cdot53 & + 58\cdot28 & + 1\cdot19. \end{array}$$

$$(20) \quad \begin{array}{cccc} & 294 & \text{RS} & \text{GS} & \text{V} \\ & 100 & = 37\cdot57 & + 59\cdot08 & + 3\cdot35. \end{array}$$

(XVII.) *Determination of the Sensation Values in the Blue-Green.*

The next determinations were made with two slits, as before described; one being at SSN 245 and the other in the blue of different hues, with the following results. The first one is shown in detail. Slits at SSNs 312 and 245.

The frame was moved .9 division of the scale towards the red, which was equivalent to placing the slits at SSNs 302.4 and 241.4 respectively, the back scale being .4 of the front scale.

Now the increase in red and consequent diminution in the green sensation at 241.4 is 4.54.

The proportion of RS to GS is therefore (see Equation (6) for 100)

$$\begin{array}{cccc} \text{RS} & \text{RS} & \text{GS} & \text{GS} \\ (69\cdot60 + 4\cdot54) & \text{to} & (30\cdot40 - 4\cdot54) & \text{or } 74\cdot14 \text{ to } 25\cdot86. \end{array}$$

The luminosity equation is

$$\begin{array}{ccc} 241\cdot4 & 208\cdot4 & \text{W.} \\ 87 & + 13 & = 100. \end{array}$$

From this we derive that

$$(21) \quad \begin{array}{cccc} 308\cdot4 & \text{RS} & \text{GS} & \text{V} \\ 100 & = 30\cdot15 & + 56\cdot85 & + 13. \end{array}$$

Slits at 245 and 320.

The slit-holder was moved 5 of the back scale, which was equivalent to moving each slit 2 units towards the red. The slits were, therefore, actually at 243 and 318.

The increase in red being 1.25 per cent. per unit of scale, at this point it became 72.1 per cent. and the green 27.9 per cent.

The equation is

$$\begin{array}{ccc} 243 & 318 & \text{W} \\ 92 & + 8 & = 100. \end{array}$$

Hence

$$(22) \quad \begin{array}{cccc} 318 & \text{RS} & \text{GS} & \text{V} \\ 100 & = 26 & + 53 & + 21. \end{array}$$

Similarly the following equations were found :—

$$(23) \quad \begin{array}{cccc} 329 & \text{RS} & \text{GS} & \text{V} \\ 100 & = 18\cdot8 & + 45\cdot3 & + 35\cdot9. \end{array}$$

$$(24) \quad \begin{array}{cccc} 339\cdot6 & \text{RS} & \text{GS} & \text{V} \\ 100 & = 15 & + 30 & + 55. \end{array}$$

$$(25) \quad \begin{array}{cccc} 349\cdot75 & \text{RS} & \text{GS} & \text{V} \\ 100 & = 9\cdot7 & + 19\cdot4 & + 70\cdot9. \end{array}$$

$$(26) \quad \begin{array}{cccc} 359\cdot94 & \text{RS} & \text{GS} & \text{V} \\ 100 & = 4\cdot6 & + 9\cdot4 & + 86. \end{array}$$

$$(27) \quad \begin{array}{cccc} 370 & \text{RS} & \text{G} & \text{V} \\ 100 & = 0 & + 3 & + 97. \end{array}$$

At 380 the violet was of the same hue as further in the spectrum.

This completes the observations made in the spectrum with the provisional violet sensation. It now remains to show how the composition of the violet was determined.

(XVIII.) *Determination of the Composition of the Violet.*

A slit was placed at SSN 205 and another at SSN 345, and mixture made to match a violet at SSN 400, to which white was added.

The equation was

$$\begin{array}{cccc} \text{B} & \text{R} & \text{V} & \text{W} \\ 33 & + 15\cdot2 & = 21\cdot2 & + 27, \end{array}$$

$$\begin{array}{ccc} \text{V} & \text{R} & \text{BS} \\ 21\cdot2 & = 15\cdot2 & + 6, \end{array}$$

or

$$(28) \quad \begin{array}{ccc} \text{V} & \text{RS} & \text{BS} \\ 100 & = 71\cdot7 & + 28\cdot3. \end{array}$$

Other equations made at 230, 235, 240, 250, gave the following :—

$$(29) \quad \begin{array}{ccc} \text{V} & \text{RS} & \text{BS} \\ 100 & = 70 & + 30. \end{array}$$

$$(30) \quad \begin{array}{ccc} \text{V} & \text{RS} & \text{BS} \\ 100 & = 72 & + 28. \end{array}$$

$$(31) \quad \begin{array}{ccc} \text{V} & \text{RS} & \text{BS} \\ 100 & = 74\cdot5 & + 25\cdot5. \end{array}$$

$$(32) \quad \begin{array}{ccc} \text{V} & \text{RS} & \text{BS} \\ 100 & = 73\cdot5 & + 26\cdot5. \end{array}$$

The adopted reading was

$$(33) \quad \begin{array}{ccc} & V & RS \quad BS \\ 100 & = & 72.5 + 27.5. \end{array}$$

(XIX.) *Corrected Colour Sensations.*

TABLE I.

This equation was applied to the foregoing percentages of violet in the different colours. The next table shows the provisional and the correct percentages.

In this and the following tables the former are shown in *italics*.

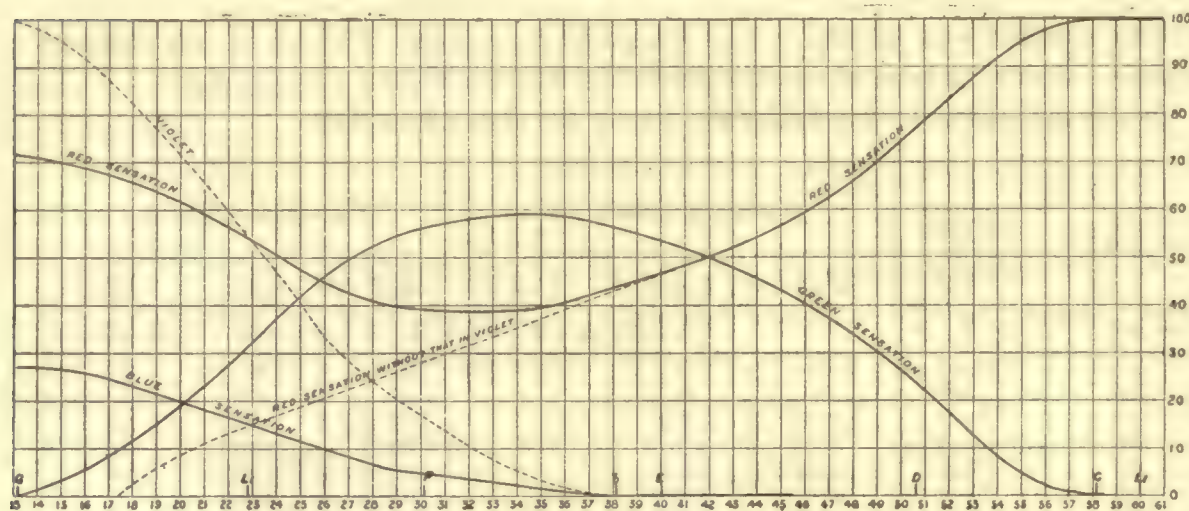
SSN.	Standard scale number.	Provisional sensations.			Corrected sensations.		
		Red.	Green.	Violet.	Red.	Green.	Blue.
205	59.83	<i>100</i>	<i>0</i>	<i>0</i>	100	0	0
215	57.07	<i>100</i>	<i>0</i>	<i>0</i>	100	0	0
220	55.70	<i>97.04</i>	<i>2.96</i>	<i>0</i>	97.04	2.96	0
228	53.48	<i>89.37</i>	<i>10.63</i>	<i>0</i>	89.37	10.63	0
236	51.27	<i>80.50</i>	<i>19.50</i>	<i>0</i>	80.50	19.50	0
240	50.17	<i>74.92</i>	<i>25.08</i>	<i>..</i>	74.92	25.08	<i>..</i>
245	48.80	<i>69.60</i>	<i>30.40</i>	<i>..</i>	69.60	30.40	<i>..</i>
250	47.42	<i>64.62</i>	<i>35.36</i>	<i>0.02</i>	64.63	35.26	0.01
260	44.67	<i>55.68</i>	<i>44.17</i>	<i>0.15</i>	55.79	44.17	0.04
270	41.92	<i>49.23</i>	<i>50.55</i>	<i>0.22</i>	49.38	50.55	0.07
275	40.55	<i>46.75</i>	<i>52.89</i>	<i>0.36</i>	47.01	52.89	0.10
280	39.17	<i>44.77</i>	<i>54.69</i>	<i>0.54</i>	45.16	54.69	0.15
283	38.35	<i>43.63</i>	<i>55.60</i>	<i>0.77</i>	44.18	55.60	0.22
285	37.80	<i>42.71</i>	<i>56.37</i>	<i>0.92</i>	43.37	56.37	0.26
288.5	36.83	<i>41.24</i>	<i>57.74</i>	<i>1.02</i>	41.97	57.74	0.29
290	36.42	<i>40.53</i>	<i>58.28</i>	<i>1.19</i>	41.39	58.28	0.33
294	35.32	<i>37.57</i>	<i>59.08</i>	<i>3.35</i>	40.00	59.08	1.92
308.4	31.37	<i>30.15</i>	<i>56.85</i>	<i>13.00</i>	39.57	56.85	3.58
316	28.73	<i>26.00</i>	<i>53.00</i>	<i>21.00</i>	41.22	53.00	5.78
329	25.71	<i>18.20</i>	<i>45.30</i>	<i>35.90</i>	44.83	45.30	9.87
339.6	22.78	<i>15.00</i>	<i>30.00</i>	<i>55.00</i>	54.87	30.00	15.13
349.75	20.00	<i>9.70</i>	<i>19.40</i>	<i>70.90</i>	61.10	19.40	19.50
359.9	17.17	<i>4.60</i>	<i>9.40</i>	<i>86.00</i>	66.95	9.4	23.65
370	14.42	<i>0</i>	<i>3</i>	<i>97.00</i>	70.32	3.0	26.68

Both sets of ordinates were drawn from the preceding table, and freehand curves drawn through them. (The standard scale is the same as in 'Colour Photometry,' Part III.) The results are shown in fig. 3. It will be noticed that, had the provisionally-employed violet sensation been correct, the percentage curves are very fairly regular, and altogether what would have been expected, but that in the true sensation curves the red sensation takes a form which is curious, and one which, from any theoretical considerations, would not be prophesied as probable. In every investigation, whether of colour fields or otherwise, the red sensation seems to be but little connected with the other two.

(XX.) *Sub-division of Luminosity into Sensations.*

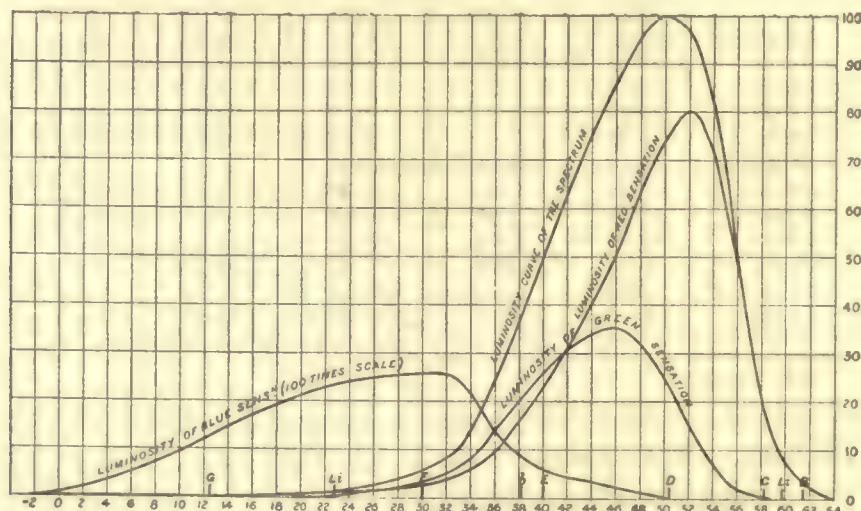
Having ascertained the percentage composition in sensation luminosity of all the spectrum, the luminosity curve of any known spectrum can be sub-divided into

Fig. 3.



Percentage of colour sensations as luminosity in the prismatic spectrum colours.

Fig. 4.



Sensation-luminosities in the spectrum of the light of the crater of the positive pole of the arc light as seen with the centre of the retina.

sensation-luminosities. This is done in the next table. Columns X., XI., XII., XIII., XIV., XV. and XVI. give the sensation-luminosity curves derived from the total luminosity curve of the spectrum of the crater of the positive pole of the arc

electric light, the ordinates for which are given in 'Colour Photometry,' Part III. The graphic results are shown in fig. 4. In this figure the blue sensation curve ordinates are on a scale 100 times larger than those of the red and green sensations. The luminosity of this blue sensation is really very small, and except for the hue would be negligible.

The areas of the sensation curves in this figure, or of one constructed with the RS, GS, and VS, should, supposing the white light to be the same as that used in the observations, be proportional to the constants in the colour equations for white light. The areas of the RS, GS, and VS curves are closely 1102, 529, and 247 on an empiric scale, and these numbers, converted into percentages, give

$$\begin{array}{cccc} \text{RS} & \text{GS} & \text{V} & \text{W} \\ 66.55 + 31.96 + 1.49 = 100. \end{array}$$

The equation employed is

$$\begin{array}{cccc} \text{RS} & \text{GS} & \text{V} & \text{W} \\ 68.42 + 29.90 + 1.68 = 100. \end{array}$$

Owing to the colour of the glass interposed in the beam, and to the slightly different angular dimension on the retina of the images in the measurements on the two occasions, this small discrepancy is fully accounted for. To see whether experiments bear out this deduction, a measure was made under the conditions which were present when the curves in 'Colour Photometry,' Part III., were made, and it came out as follows—

$$\begin{array}{cccc} \text{RS} & \text{GS} & \text{V} & \text{W} \\ 66.20 + 32.28 + 1.52 = 100. \end{array}$$

This is sufficiently close to indicate that the measurements made are fairly exact.

TABLE II.—Table showing Results of Applying Table I. to the Luminosity Curve of the Spectrum as Measured on the Yellow Spot of the Retina.

I. Scale num- ber of spec- trum.	II. SSN.	III. λ .	IV. Percentages of luminosity of			VII. Final percentages of			X. Lumi- nosity of spec- trum colours.	XI. Luminosity of pris- matic spectrum colours sub-divided into luminosities of			XIV. Luminosity of pris- matic spectrum colours sub-divided into luminosities of			XVII. Equal ordinates to make white.			XIX.
			RS.	GS.	VS.	RS.	GS.	BS.		RS.	GS.	VS.	RS.	GS.	BS.	RS.	GS.	BS.	
64	...	7217	100	0	0	100	0	0	0.5	0.5	0.5	0.5
63	...	7082	100	0	0	100	0	0	1	1	1	1
62	...	6957	100	0	0	100	0	0	2	2	2	2
61	198.73	6839	100	0	0	100	0	0	4	4	4	4
60	204.36	6728	100	0	0	100	0	0	7	7	7	7
59	208.00	6621	100	0	0	100	0	0	12.5	12.5	12.5	12.5
58	211.64	6520	99.5	0.5	0	99.5	0.5	0	21	20.89	1.05	...	20.89	0.22	...	20.89	0.22
57	215.28	6423	99	1	0	99	1	0	33	32.67	0.33	...	32.67	0.67	...	32.67	0.67
56	218.92	6330	98	2	0	98	2	0	50	49.00	1.00	...	49.00	2.13	...	49.00	2.13
55	222.55	6242	95.5	4.5	0	95.5	4.5	0	65	62.05	2.95	...	62.05	6.25	...	62.05	6.25
54	226.19	6152	92	8.0	0	92	8.0	0	80	73.6	6.40	...	73.6	13.56	...	73.6	13.56
53	229.73	6074	88	12.0	0	88	12.0	0	90	79.2	10.80	...	79.2	22.90	...	79.2	22.90
52	233.36	5996	83	17	0	83	17.0	0	96	79.58	16.42	...	79.58	34.80	...	79.58	34.80
51	237.00	5919	79	21	0	79	21	0	99	78.22	20.79	...	78.22	44.08	...	78.22	44.08
50	240.64	5850	74	26	0.005	74	26	0.001	100	74.00	26.00	0.005	74.00	55.12	0.16	74.00	55.12	0.16	...
49	244.27	5783	70	30	0.015	70	30	0.004	99	69.30	29.69	0.015	69.31	62.96	0.66	69.31	62.96	0.66	...
48	247.91	5720	66.5	33.5	0.03	66.51	33.5	0.008	97	64.50	32.47	0.030	64.52	68.73	1.32	64.52	68.73	1.32	...
47	251.55	5658	62.7	37.2	0.05	62.73	37.2	0.013	92.5	58.00	34.45	0.050	58.03	73.02	2.47	58.03	73.02	2.47	...
46	255.18	5596	59.2	40.7	0.08	59.26	40.7	0.022	87	51.50	35.43	0.071	51.55	75.11	3.54	51.55	75.11	3.54	...
45	258.83	5538	56.2	43	0.11	56.28	43.0	0.03	81	45.52	35.39	0.089	45.58	75.02	3.96	45.58	75.02	3.96	...
44	262.46	5481	53.7	46.2	0.15	53.81	46.2	0.04	75	40.27	34.61	0.112	40.35	73.37	5.11	40.35	73.37	5.11	...
43	266.10	5427	51.2	48.6	0.20	51.54	48.6	0.06	69	35.33	33.67	0.138	35.43	71.38	6.27	35.43	71.38	6.27	...
42	269.73	5373	49.5	50.3	0.26	49.69	50.3	0.07	62.5	30.94	31.40	0.162	31.06	66.56	7.59	31.06	66.56	7.59	...
41	273.37	5321	47.7	52.0	0.34	48.50	52.0	0.095	57	27.19	29.62	0.194	27.33	62.75	8.74	27.33	62.75	8.74	...
40	277.01	5270	46.0	53.5	0.46	46.34	53.5	0.12	50	23.00	26.75	0.230	23.16	56.71	10.39	23.16	56.71	10.39	...
39	280.64	5221	44.5	54.9	0.60	45.44	54.9	0.165	42.5	18.91	23.33	0.255	19.09	49.46	11.55	19.09	49.46	11.55	...
38	284.28	5172	43.38	56.4	0.80	43.38	56.4	0.22	36.0	15.41	20.30	0.288	15.62	43.03	13.20	15.62	43.03	13.20	...
37	287.92	5128	41.2	57.7	1.1	42.00	57.7	0.30	29.5	12.15	17.05	0.324	12.38	36.14	14.85	12.38	36.14	14.85	...
36	291.55	5085	39.3	58.9	1.8	40.6	58.9	0.50	24	9.43	14.09	0.432	9.74	29.90	19.8	9.74	29.90	19.8	...

TABLE II. (continued).—Table showing Results of Applying Table I. to the Luminosity Curve of the Spectrum as measured on the Yellow Spot of the Retina.

I.	II. Scale num- ber of spec- trum.	III. A.	IV. Percentages of luminosity of			VII. Final percentages of			X. Lumi- nosity of spec- trum colours.	XI. Luminosity of pris- matic spectrum colours sub-divided into luminosities of			XIV. Luminosity of pris- matic spectrum colours sub-divided into luminosities of			XVII. XVIII. XIX. Equal ordinates to make white.		
			RS.	GS.	VS.	RS.	GS.	BS.		RS.	GS.	VS.	RS.	GS.	BS.	RS.	GS.	BS.
35	295.19	5043	37.0	59.0	3.6	39.6	59.0	1.00	18.4	6.81	11.06	0.662	7.28	11.04	.183	7.28	23.44	30.2
34	298.83	5002	35.0	59	5.5	39	59.0	1.5	14.2	4.97	8.38	0.781	5.53	8.38	.215	5.53	17.54	35.47
33	302.47	4963	33.0	58.5	7.5	39.4	52.5	2.1	10.5	3.46	6.15	0.892	4.10	6.15	.245	4.10	13.04	40.40
32	306.10	4924	31.0	58	11	39	58.0	3.0	8.5	2.63	4.93	0.935	3.30	4.93	.257	3.30	10.45	42.40
30	313.38	4848	27.0	56.0	17	39.3	56.0	4.7	5.7	1.48	3.08	0.969	2.18	3.08	.268	2.18	6.53	44.00
28	320.65	4776	23.5	52.5	24	40.9	53.5	6.6	4	.940	2.10	0.900	1.63	2.10	.265	1.63	4.45	43.23
26	327.92	4707	19.7	46.8	33.5	44.0	46.8	9.2	2.8	.55	1.31	0.938	1.23	1.31	.257	1.23	2.78	42.40
24	335.19	4639	16.0	37	48	50.3	37	12.9	1.9	.35	.60	0.893	.99	.60	.245	.99	1.23	40.43
22	342.47	4578	12.5	27.5	60	56.0	27.5	16.5	1.4	.17	.29	0.840	.88	.29	.233	.88	.63	38.44
20	349.73	4517	9.5	19.0	71.5	61.5	19.0	19.5	1.1	.10	.22	0.786	.67	.22	.213	.67	.47	35.14
18	357.00	4459	6	11.5	82.5	66	11.5	22.5	.86	.05	.11	0.761	.56	.11	.193	.56	.23	32.21
16	364.25	4404	2.5	5.0	92.5	69.5	5.0	25.5	.70	.01	.05	0.647	.47	.05	.178	.47	.10	29.37
14	371.50	4349	0	2.0	98	71	2.0	27.0	.56	0	.01	0.548	.39	.01	.155	.39	.02	25.57
12	378.75	4296	0	0.5	99.5	72.1	0.5	27.4	.45	0	0	0.445	.32	0	.127	.32	0	20.95
10	386.00	4245	0	0	100	72.5	0	27.5	.34	0	0	0.34	.25	0	.092	.25	0	15.1
8	393.27	4197	0	0	100	72.5	0	27.5	.26	0	0	0.26	.19	0	.075	.19	0	12.1
6	400.52	4151	0	0	100	72.5	0	27.5	.18	0	0	0.18	.13	0	.050	.13	0	8.5
4	407.25	4106	0	0	100	72.5	0	27.5	.14	0	0	0.14	.10	0	.039	.10	0	6.6
2	...	4060	0	0	100	72.5	0	27.5	.10	0	0	0.10	.07	0	.023	.07	0	4.4

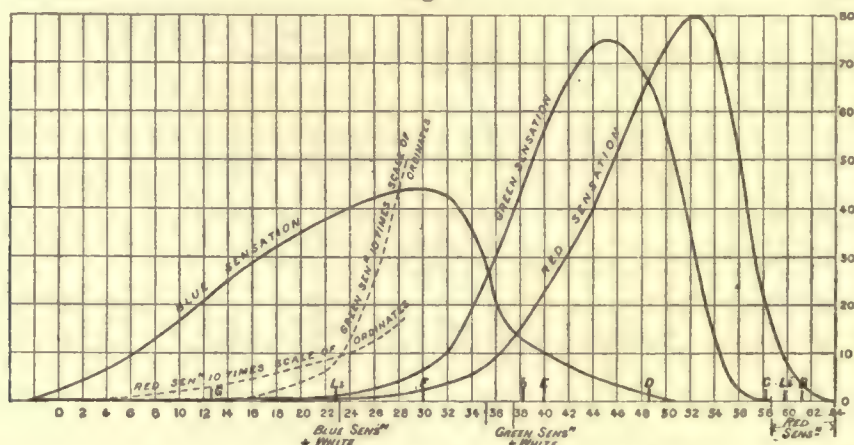
(XXI.) *Curves showing Equal Ordinates of Red, Green, and Blue Sensations to give White Light.*

The equation derived from the foregoing areas being taken as correct, when the blue sensation replaces the violet, the final equation becomes

$$\begin{array}{cccc} \text{RS} & \text{GS} & \text{BS} & \text{W} \\ 67\cdot63 + 31\cdot96 + \cdot41 = 100, \end{array}$$

and we can find the curves which will have ordinates on such a scale that, when equal, they give white. Taking the red curve as the standard, we must multiply the GS ordinates by $\frac{67\cdot63}{31\cdot96}$, or 2·12, to make the areas of the two equal. When equal, the desired result is obtained as far as the green sensation is concerned. The BS ordinates must be multiplied by $\frac{67\cdot63}{\cdot41}$, or 165, to obtain the result for the third curve. These new ordinates are shown in Columns XVIII. and XIX., Table II., and these, with Column XVII., are shown graphically in fig. 5.

Fig. 5.



Sensation curves (prismatic spectrum) in which equal heights of ordinates form white.

From these curves can be seen at a glance the positions that A and D, fig. 1, occupy, and they show also those parts of the spectrum where the green and blue sensations are seen, unmixed with any other sensation except white. These positions of A and D we find to be about Scale Nos. 37·3 and 35·2, which are λ 5120 and 5060 respectively. The purest green sensation is felt at the former Scale Number, and the purest blue sensation is at Scale No. 23·2, or close to the blue lithium line, which is at Scale No. 22·8. As before said, the light of the crater is of that "whiteness" which closely matches the white outside the colour fields; hence it may be surmised that at these two points we have the nearest approach to the true green and blue sensations.

(XXII.) *Confirmation of the Observations by Colour-blind Persons.*

In confirmation of the positions of A and D, fig. 1, as stated before, complete red- and green-blind eyes were called in to make observations. A totally green-blind person gave the following readings for that position in the spectrum where white was matched. The Scale Numbers used are those of the diagram.

The white was placed alongside the spectrum colours, and the slit through which the colour issued was gradually moved from the red towards the neutral point. The same procedure was adopted in moving from the blue towards the same point.

The readings were

From the red.				From the blue.		
38·5,	37·5,	38,	37·1	36·8,	37·1,	37·5.

The mean of these readings is 37·7 as the neutral point of the green-blind. The difference is only ·2 of the scale. A look at the curve will show that there is likely to be greater variation when moving the slit from the red, as the curve is there less steep. A mean of the readings "from the blue" gives 37·1, the position fixed by the preliminary trials, and which answers to SSN 288·5.

Two red-blind persons marked the point in the spectrum where the colour matched white. One read 34·2, 35, 35·4, or a mean of 35·1; the other read 35·2, 35, 35·6, 35·8, or a mean of 35·4. The mean of the two means is 35·2.

From the coincidence of the areas with the colour equations, and from the position of neutral points of the colour-blind with the points where the curves met, we may conclude that the observations are correct within the limits of the errors of observation.

It may be stated that the nearest approaches to the colour sensations in pigments are: Vermilion, to which a little blue has been added; emerald green and true ultramarine, to which a slight trace of red has been added. GREVILLE'S cyanine blue is not far from the colour. All are slightly paler, however, and in using them as colour discs this paleness must be allowed for.

(XXIII.) *The Observations applied to the Normal Spectrum of the Electric Arc Light.*

Before proceeding further, I have thought that it would be of interest to show the colour sensations of a normal spectrum. The compression of the red in the prismatic spectrum and the extension of the blue does not enable a comparison to be easily made between the sensation curves of this spectrum and the results obtained by KENIG, which are based on the normal spectrum.

The following table is calculated from observations made with a grating spectrum in 1891. The grating was ruled on speculum metal, and had about 14,000 lines to the inch.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
λ .	Percentage luminosity.			Lumi- nosity of spec- trum.	Sub-division of spectrum luminosity into luminosities of			Equal ordinates to give white.		
	RS.	GS.	BS.		RS.	GS.	BS.	RS.	GS.	BS.
7100	100	0	0	0.5	0.5	0.5
7000	100	0	0	0.9	0.9	0.9
6900	100	0	0	1.6	1.6	1.6
6800	100	0	0	3.2	3.2	3.2
6700	100	0	0	6.0	6.0	6.0
6600	99.8	0.2	0	10.0	9.9	0.1	...	9.9	0.22	...
6500	99	1.0	0	17.0	16.8	0.2	...	16.8	0.44	...
6400	98	2.0	0	26.0	25.48	0.52	...	25.48	1.13	...
6300	97	3.0	0	41	39.77	1.23	...	39.77	2.67	...
6200	94	6.0	0	59	55.46	3.54	...	55.46	7.68	...
6100	89.5	10.5	0	75	67.13	7.87	...	67.13	17.08	...
6000	83.3	16.7	0	85	70.81	14.19	...	70.81	30.79	...
5900	77.5	22.5	0	93	72.08	20.92	...	72.08	45.39	...
5800	71.3	28.7	0.005	99	70.38	28.42	.005	70.38	61.67	0.7
5700	65.3	35.0	0.01	100	65.00	35.00	.01	65.00	75.95	1.4
5600	59.3	40.5	0.023	95	56.52	38.46	.02	56.52	83.45	2.9
5500	54.3	45.7	0.040	89	48.33	40.64	.035	48.33	90.19	4.9
5400	49.7	50.2	0.065	80	39.76	40.16	.052	39.76	87.15	7.38
5300	47.2	52.7	0.11	70	33.04	36.58	.077	33.04	79.37	10.93
5200	53.6	56.2	0.18	56	24.00	29.90	.099	24.00	64.88	14.10
5100	41.2	58.4	0.42	35	14.42	20.43	.147	14.42	44.33	20.87
5000	39.3	59.0	1.6	18	7.09	10.61	.300	7.09	23.02	40.89
4900	39.0	57.5	3.5	11	4.48	6.50	.385	4.48	14.10	54.60
4800	40.0	54.0	6.0	7.5	3.00	4.05	.456	3.00	8.79	64.75
4700	45.0	44.8	10.2	5.0	2.25	2.24	.510	2.25	4.88	71.00
4600	54.5	30.0	15.5	3.5	1.90	1.06	.542	1.90	2.30	76.9
4500	63.5	16.0	20.5	2.7	1.71	0.44	.553	1.71	0.95	78.5
4400	69.8	4.5	25.7	2.1	1.47	0.09	.540	1.47	0.20	76.68
4300	72.5	0	27.5	1.7	1.23	0	.470	1.23	0	66.74
4200	72.5	0	27.5	1.3	.94	0	.357	.94	0	50.69
4100	72.5	0	27.5	1.0	.72	0	.275	.72	0	39.05
4000	72.5	0	27.5	.75	.54	0	.206	.54	0	29.25
3900	72.5	0	27.5	.50	.36	0	.137	.36	0	19.45
3800	72.5	0	27.5	.25	.18	0	.068	.18	0	9.22

Column I. shows the wave-lengths; Columns II., III., and IV. the percentage luminosity of the sensations (see fig. 6); Column V. the luminosity; Columns VI., VII., and VIII. the luminosity of the sensations in the normal spectrum. The approximate areas of the three curves shown in Columns VI., VII., and VIII., and graphically in fig. 7, are 747.6, 344.3, and 5.3 for the RS, GS, and BS respectively, and the equation for white is

$$\begin{array}{cccc} \text{RS} & \text{GS} & \text{BS} & \text{W} \\ 68.14 + 31.38 + .48 = 100. \end{array}$$

Columns VII. and VIII. have to be multiplied by $\frac{68.14}{31.32}$ and $\frac{68.14}{.48}$, or 2.17 and 142

respectively, to give equal areas with the RS area in Column VI. Column IX. is Column VI. repeated, and Columns X. and XI. show the curves for the GS and BS when of equal areas, hence the ordinates, when equal, give white. These last curves are shown in fig. 8. The above equation is not very different from that obtained

Fig. 6.

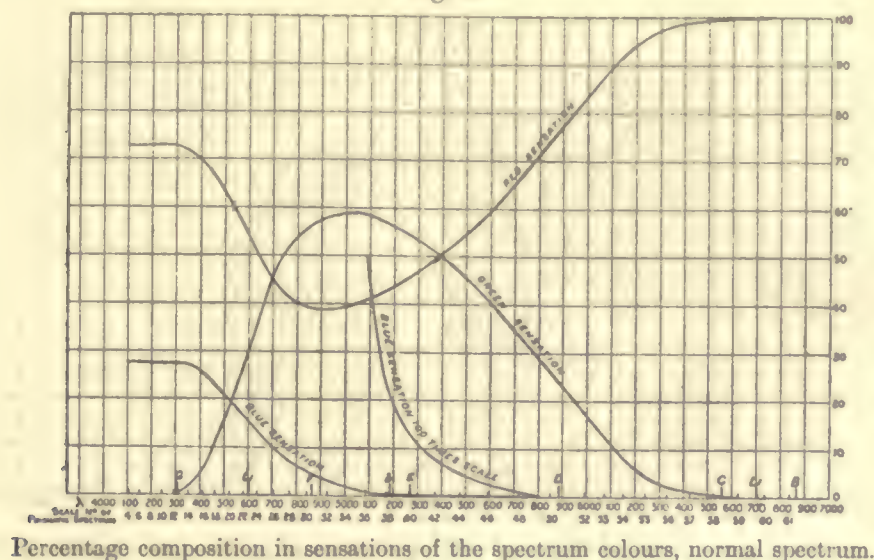
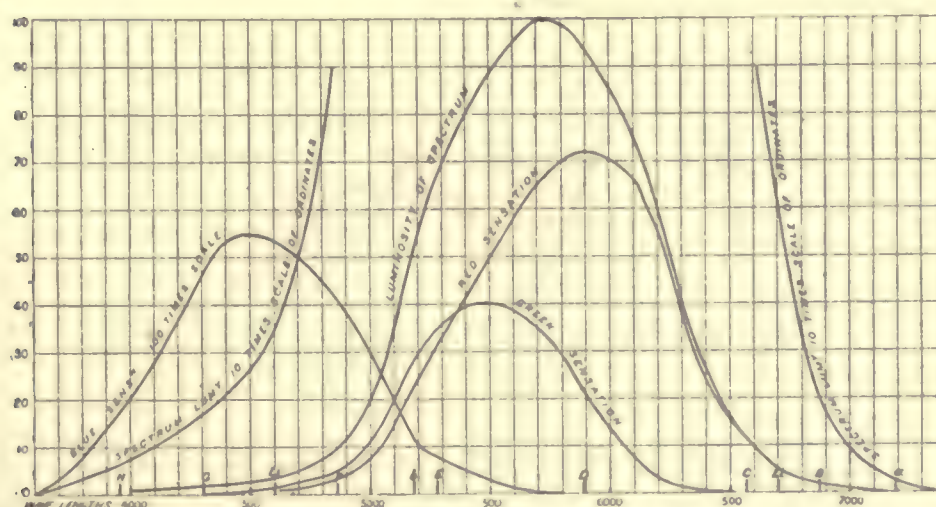


Fig. 7.

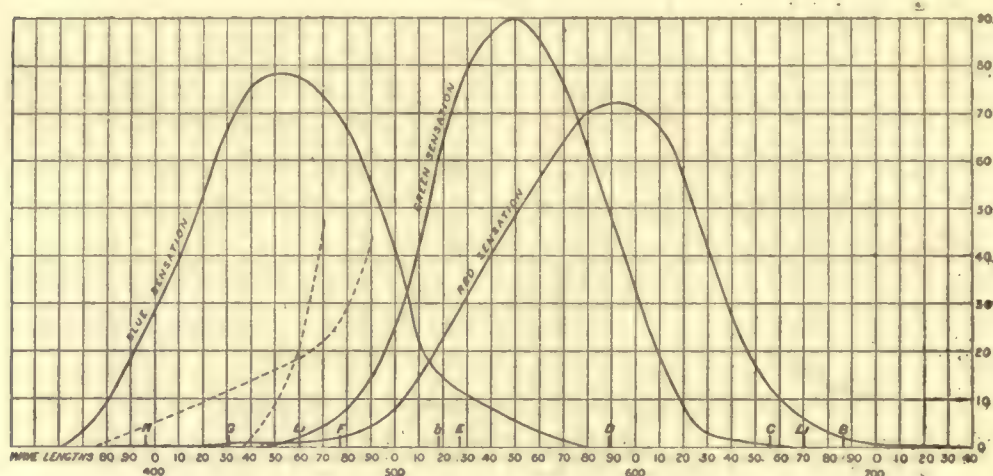


from the prismatic spectrum of the same light. Any difference is caused in all probability by the colour of the light reflected by the grating, together with that caused by the necessary error of observation.

A comparison of the curves in figs. 5 and 8 shows what an effect the compression and extension of the red and blue of the spectrum has on the shape and appearance

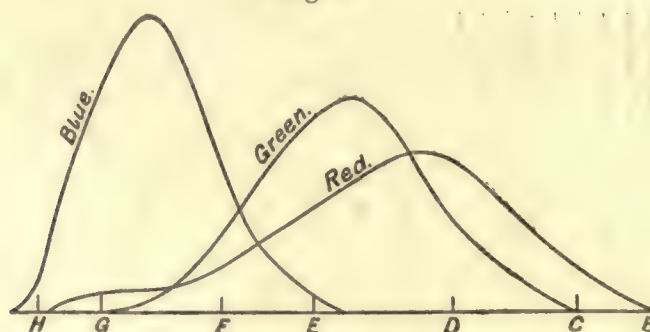
of the curves, and how they approach in some respects those of KÆNIG's, of which fig. 9 is a rough representation taken from one of his diagrams. There is a marked difference, however, in the amount of red shown as existing in the violet. Whatever source of light is taken as the standard the same proportion will exist.

Fig. 8



Sensation curves (normal spectrum) in which equal heights of ordinates form white (electric light crater).

Fig. 9.



(XXIV.) *Observation applied to the Solar Spectrum.*

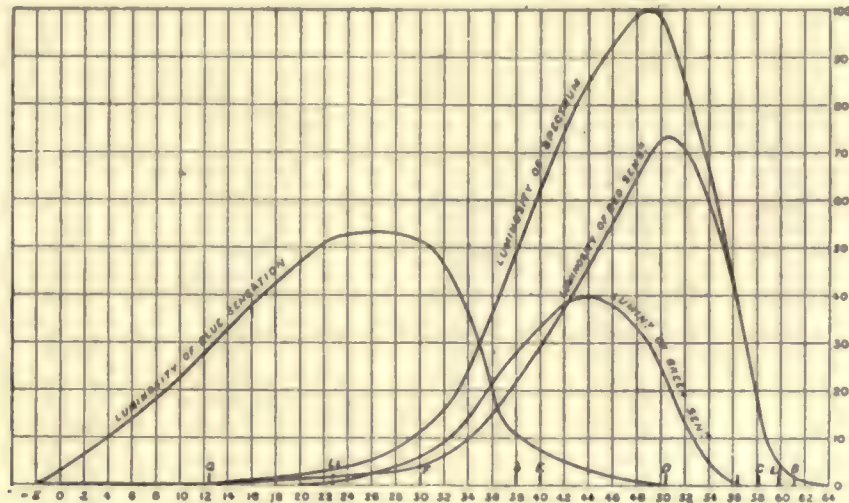
One more example may be given. The sun's spectrum in the month of September, at noon, was measured several years ago, and this has been divided up into luminosities. It is very similar in characteristics to the electric light spectrum. The equation to the white light derived from the areas is

$$\begin{array}{cccc} \text{RS} & \text{GS} & \text{BS} & \text{W} \\ 65.73 & + & 33.83 & + .44 = 100. \end{array}$$

The green sensation is more stimulated by this light than it is in the electric light, whilst curiously enough the blue sensation appears to be very much the same (fig. 10).

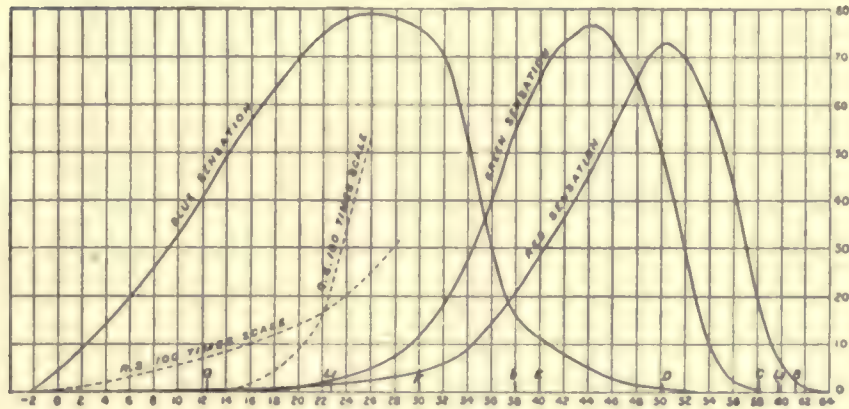
To reduce the curves to equal areas the green sensation has to be multiplied by 1.94 and the blue by 149. These are given in Columns VI., VII., and VIII. of the table and are graphically shown in fig. 11.

Fig. 10.



Sensation luminosity in sunlight of noon in September.

Fig. 11.



Sensation curves (prismatic spectrum) in which equal heights of ordinates form white (sun light).

SENSATION Curves in Sun's Spectrum.

I. Scale number.	II. Luminosity.	III. IV. V. Percentage composition.			VI. VII. VIII. Curves of equal areas.		
		RS.	GS.	BS.	RS.	GS.	BS.
64	0	0	0
63	0.5	0.5	0.5
62	0.74	0.74	0.74
61	2.5	2.5	2.5
60	4.5	4.5	4.5
59	9.0	9.0	9.0
58	19.0	18.9	0.1	...	18.9	0.19	...
57	32.0	31.68	0.32	...	31.68	0.62	...
56	43.0	42.14	0.86	...	42.14	1.67	...
55	55	52.52	2.48	...	52.52	4.81	...
54	64	58.88	5.12	...	58.88	9.93	...
53	75	66.00	9.00	...	66.00	17.46	...
52	85	70.55	14.45	...	70.55	28.03	...
51	93	73.47	19.53	...	73.47	37.89	...
50	98	72.62	25.38	.001	72.62	48.24	0.148
49	100	70.00	30.00	.004	70.00	58.20	0.592
48	98.5	65.42	33.00	.008	65.42	64.02	1.184
47	95.5	59.94	35.55	.012	59.94	68.97	1.776
46	93.5	55.40	38.08	.021	55.40	73.87	3.108
45	90	50.34	39.63	.027	50.34	76.88	3.996
44	85	45.74	39.23	.034	45.74	76.10	5.032
43	80.2	41.17	38.98	.048	41.17	75.62	7.104
42	75.5	37.31	38.14	.053	37.31	73.99	7.844
41	69.5	33.32	36.11	.066	33.32	70.05	9.768
40	63.0	28.52	33.73	.075	28.52	65.44	11.100
39	56.5	25.69	31.02	.093	25.69	60.18	13.764
38	50	21.69	28.20	.110	21.69	54.71	16.280
37	43.5	18.27	25.10	.130	18.27	48.69	19.244
36	36.5	14.82	21.03	.200	14.82	40.80	29.600
35	30.0	11.88	17.82	.300	11.88	34.57	44.40
34	24	9.36	14.28	.360	9.36	27.70	53.28
33	19	7.48	11.12	.399	7.48	21.57	59.05
32	16	6.24	9.28	.480	6.24	18.00	71.04
30	11	4.32	6.16	.517	4.32	11.95	76.52
28	7.8	3.19	4.08	.529	3.19	7.91	78.29
26	5.85	2.57	2.75	.533	2.57	5.33	78.88
24	4.1	2.06	1.51	.529	2.06	2.93	78.29
22	3.1	1.73	0.85	.511	1.73	1.64	75.63
20	2.3	1.41	0.42	.470	1.41	0.81	69.56
18	1.9	1.25	0.22	.427	1.25	0.43	63.20
16	1.5	1.04	0.08	.382	1.04	0.15	56.54
14	1.24	0.88	0.03	.335	0.88	0.08	49.58
12	1.03	0.73	0.02	.282	0.73	0.04	41.74
10	0.80	0.58	0	.220	0.58	0	32.56
8	0.66	0.48	0	.180	0.48	0	26.60
6	0.51	0.37	0	.140	0.37	0	20.70
4	0.36	0.26	0	.100	0.26	0	14.80
2	0.23	0.16	0	.070	0.16	0	10.40

In fig. 10 it will be noticed that A and D of fig. 1 are somewhat closer together, and that the place where the blue sensation exists mixed with white alone, is again close to the blue lithium line. The blue sensation curve is also somewhat higher.

Confirmatory of these curves are the luminosity curves given for the red blind in 'Colour Photometry,' Part III. If the curves there given be reduced to a little more than one-half the scale of ordinates, they will be found to closely correspond to those of fig. 4. It must be remembered that to them the red luminosity is non-existent throughout the spectrum, hence the luminosity of the violet end is much diminished. For this reason the luminosity curves were made on too high a scale when drawn for that paper, and they should be corrected accordingly. It need not follow from this investigation that the colour-blind see less light than those having the three full sensations, though the "extinction" readings given in that same paper seem to indicate that such is the case. A further investigation into this is in hand, and for the present the question must be left an open one.

I have to thank my assistant, Mr. WALTER BRADFIELD, for the aid he has given me in this investigation. The actual observations recorded were made by myself, but all preparatory work was done by him.

IX. *On the Comparative Efficiency as Condensation Nuclei of Positively and Negatively Charged Ions.*

By C. T. R. WILSON, M.A.

Communicated by the Meteorological Council.

Received May 11,—Read June 15, 1899.

THE work, of which the results are given in this communication, forms part of an investigation on atmospheric electricity, on which I am engaged on behalf of the Meteorological Council.

The relation between rain and atmospheric electricity was one of the problems it was suggested I should study experimentally. The importance in connection with that question of the subject dealt with in this paper has already been noticed by Professor J. J. THOMSON, who points out* that “if the negative ions, say, were to differ in their power of condensing water around them from the positive, then we might get a cloud formed round one set of ions and not round the other. The ions in the cloud would fall under gravity, and thus we might have separation of positive and negative ions and the production of an electric field, the work required for the production of the field being done by gravity.”

To make this process worthy of consideration as a source of atmospheric electricity, it would be necessary to show reason for believing (1) that atmospheric air in the regions in which rain is formed is likely to contain free ions, (2) that the positively and negatively charged ions differ in their efficiency as condensation nuclei.

With respect to the first of these questions, former experiments furnish considerable evidence in favour of an affirmative answer. When moist dust-free air is allowed to expand suddenly, a slight rain-like condensation always takes place if the maximum supersaturation attained exceeds a certain limit. This limit is identical with that which is necessary for the formation of fogs in air, in which a supply of ions has been produced by the action of Röntgen rays or other ionising agent. The nuclei, on which the drops are formed in air exposed to the rays, were shown experimentally to be identical with the ions to which the conductivity of the gas when exposed to the rays is due. The equality of the expansion required to give the comparatively few drops in the absence of the rays, with that required to cause water to condense on the ions, is so exact as to furnish what is at first sight almost convincing evidence

* ‘Phil. Mag.,’ December, 1898, p. 533

that ordinary moist air is always to a very slight extent ionised. The number of these nuclei is so small that the absence of any sensible conductivity in air under ordinary conditions is in no way inconsistent with the view that they are ions. In the latter part of this paper are described some attempts which I have made to decide experimentally whether these nuclei are charged or not.

It is mainly, however, with the second of the above questions that this paper deals. The experiments to be described prove that there is a great difference between positively and negatively charged ions, with respect to their power of serving as nuclei for the condensation of water vapour; a much smaller degree of supersaturation sufficing to cause water to condense on the negative ions than is required in the case of positively charged ions. They therefore furnish a possible explanation of the preponderance of negatively electrified rain,* which is required by theories which attribute the normal positive potential of the air to the action of precipitation.

I have shown, in a previous paper,† that the ions produced by various agents (X-rays, uranium-rays, negatively charged zinc exposed to ultra-violet light) are identical with respect to the minimum supersaturation required to make water condense on them. They are also identical in this respect, with the few nuclei apparently always present in moist air. In the present investigation I have therefore felt justified in using exclusively the Röntgen rays as being the most convenient ionising agent, and in assuming that the same results would be obtained with ions from other sources.

To compare the efficiency as condensation nuclei of the positive and negative ions respectively, expansion experiments were made with moist air containing ions all, or nearly all, charged with electricity of one sign, alternately positive and negative in successive experiments.

To enable a supply of ions nearly all positive or nearly all negative to be produced at will in the air under observation, this was enclosed between two parallel metal plates, and a narrow beam of Röntgen rays was made to pass between the plates parallel to and almost in contact with the surface of one of them. Under these conditions a supply of positive and negative ions is produced in the thin lamina of air exposed to the rays, and when a difference of potential is maintained between the plates, the two sets of ions move in opposite directions, the positive towards the negative plate and *vice versa*. If we neglect the slight difference in the velocity of positive and negative ions, shown to exist by the experiments of ZELENY,‡ the number of ions in unit volume of the positive and negative streams will be the same, assuming (an assumption which later experiments justify) that equal numbers of positive and negative ions are produced, and that the ionisation does not, for example,

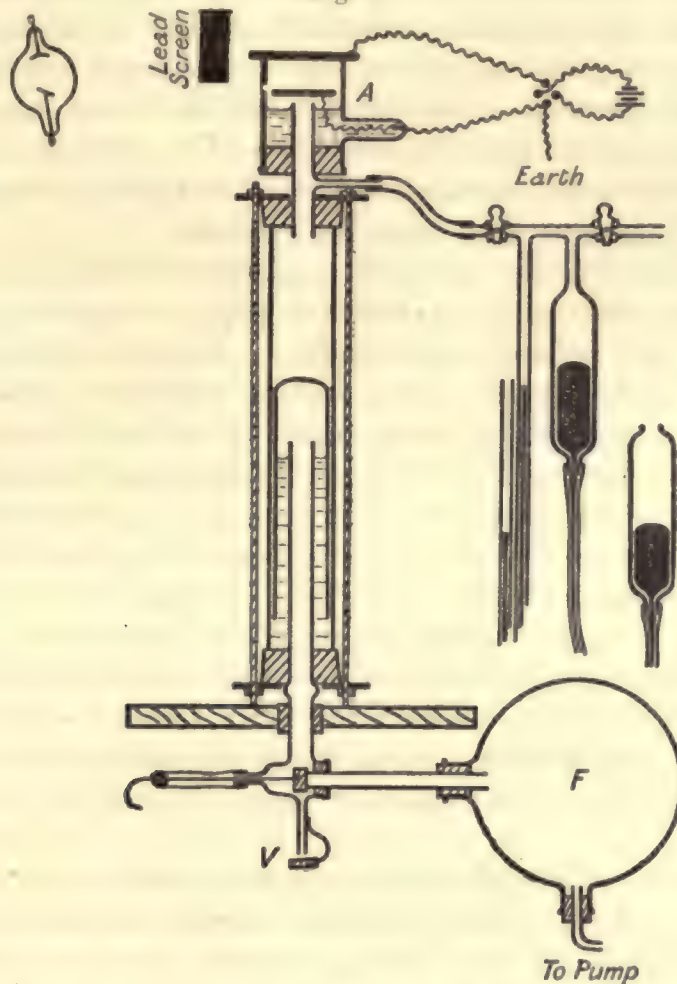
* The earlier observations of ELSTER and GEITEL appeared to show a preponderance of negatively electrified rain ('Sitzungsber. d. k. Akad. in Wien.,' 99, IIA, p. 421), but this is not shown in their later observations ('Terrestrial Magnetism,' vol. 4, p. 15).

† 'Phil. Trans.,' A, vol. 192, pp. 403-453, 1899.

‡ 'Phil. Mag.,' vol. 46, p. 120, 1898.

consist in the breaking up of the neutral molecules into a certain number of positive ions and half as many negative ions, each carrying twice as large a charge as the positive. It is plain, therefore, that there must at any moment be a great excess of the ions which have the greater distance to travel; in other words, of the ions charged with electricity of the same sign as that on the plate nearest the layer of air exposed to the rays. The expansion may either be made while this layer is exposed to the rays, or the rays may be cut off before the expansion. If the interval, between

Fig. 1.



cutting off the rays and making the expansion, lies within certain limits, it is plain that all the ions travelling to the plate next the ionised layer may have been removed, while only a small proportion of those travelling towards the more distant plate have reached it before the expansion is made. In this way we would therefore expect to get positive or negative ions with almost complete absence of ions of the other kind.

The method of producing sudden expansion of any desired amount was that which I have described in a previous paper.* Such differences as there were in the details of the apparatus are sufficiently indicated in fig. 1. The glass cylinder and piston of

* 'Camb. Phil. Soc. Proc.,' vol. 9, p. 333, 1897.

the expansion apparatus were larger than before, the former being 3·7 centims. in internal diameter. The arrangements for connecting the air-space below the piston with the vacuum in F have been improved in form, and a self-acting indiarubber valve, V, has been substituted for the stop-cock, formerly used to cut off communication with the atmosphere immediately before making this connection. The addition of this valve was found to be a great convenience.

The method of arranging for an expansion of any desired amount is described in the paper to which reference has just been made. In the new apparatus, however, an error is introduced into the measurements of expansion by the yielding of the indiarubber stoppers closing the top of the expansion cylinder and the bottom of the vessel, A, in which the clouds are observed, as well as to some extent probably by the momentum acquired by the air in the connecting tube. Both sources of error tend to make the actual maximum expansion of the air in A greater than that obtained by calculation from its pressure before and after expansion.

Now the older experiments,* made with apparatus suitable for absolute measurements, showed that there are two well-defined critical values of the expansion, which we may use as fixed points to standardise an expansion apparatus unsuited for absolute measurements. At the first point the expansion (measured by v_2/v_1 , the ratio of the final to the initial volume) is equal to 1·25; it is the minimum expansion required to make condensation in the form of drops begin in dust-free air initially saturated, whether the air be exposed to an ionising agent, such as Röntgen rays, or not. At the second point the transition from rain-like to cloud-like condensation (in the absence of ionising agents) takes place; v_2/v_1 is equal here to 1·38.

On testing the apparatus in this way the following results were obtained:—

- (1.) The air being exposed to Röntgen rays, condensation was first observed when the apparent value of $v_2/v_1 = 1·22$ instead of 1·25. Error = —·03.
- (2.) The change from rain-like to cloud-like condensation (in the absence of ionising agents) took place when the apparent value of $v_2/v_1 = 1·35$ instead of 1·38. Error = —·03.

Thus the correction to be added to the apparent values of v_2/v_1 is the same at both points and equal to +·03. I have, therefore, assumed that the same correction holds for intermediate values of v_2/v_1 . Throughout the paper the corrected values of v_2/v_1 are given.

The vessel, A, in which the ions were produced and the clouds formed upon them observed, consisted of a wide glass tube, 4·2 centims. in diameter, closed above by a brass plate, cemented to the ground top of the tube with sealing wax; 2 centims. below this plate was a smaller circular brass plate, 3·7 centims. in diameter, fixed horizontally within the tube by means of three projecting tags cemented to the sides of the tube. In the side of the tube a horizontal slot was cut, 3 centims. long and 3·5 millims. in diameter, the lower edge of the slot being on a level with the upper

* 'Phil. Trans.,' A, vol. 189, p. 265, 1897.

surface of the lower plate. The slot was closed externally by a strip of thin aluminium, cemented to the glass with shellac. A focus bulb, giving out Röntgen rays, was fixed with the anticathode on a level with the upper surface of the lower plate, the anticathode being placed with its plane almost horizontal, so that the effective source of the rays which entered the slot was almost linear. A thick lead screen was fixed, as shown in the figure, to prevent any rays reaching the interior of the vessel above the level of the slot. There is thus only a thin layer of air, close to the surface of the lower plate, exposed to the direct action of the rays from the bulb. The lower plate was kept at zero potential, while the upper plate could be connected either to the positive or negative terminal of a battery, of which the other terminal was earthed. The vessel could thus be charged at will with an excess of either positive or negative ions.

All the metal surfaces within the tube were covered with wet filter paper, to keep the air saturated with water vapour, and to prevent nuclei being produced by the action of the metal itself.

A considerable advantage is gained by having the plates horizontal, and the ionised layer in contact with the lower plate, for any drops formed on the ions which are in a minority (these being confined to the lower part of the tube), have thus only a short distance to fall, and if condensation takes place on these ions only, the drops will be confined to the lower part of the vessel.

In the experiments first performed with this apparatus the expansions were made without previously cutting off the rays.

The apparatus being adjusted to give expansions somewhat exceeding the limit $v_2/v_1 = 1.25$, comparatively dense fogs were obtained when the upper plate was maintained at a potential a few volts higher than the lower, so that negative ions were present in excess; whereas, when the field was reversed (the positive ions being now in excess) only a slight condensation could be observed, and this was mainly confined to the region immediately over the lower plate, where a considerable number of negative ions must have been present. With expansions as great as $v_2/v_1 = 1.35$ the appearance of the fogs obtained was independent of the direction of the field, and this continued to be the case up to the limit 1.38, at which dense fogs appear even in the absence of ions. With the field in the direction which gives an excess of negative ions, the density of the fogs which result from expansion is practically the same for all values of v_2/v_1 between 1.28 and the above-mentioned limit 1.38. When, on the other hand, the upper plate is connected to the negative pole of the battery, so that the positive ions are in excess, the drops remain few till v_2/v_1 amounts to about 1.31, when the number of the drops begins to increase as the expansion is increased. With $v_2/v_1 = 1.33$, we obtain, with the positive ions, comparatively dense fogs, still, however, considerably less dense than those obtained with negative ions. Finally, above 1.35 the positive and negative fogs are indistinguishable.

These results admit of only one interpretation; condensation takes place on some

of the negative ions when v_2/v_1 amounts to 1.25, practically all the negative ions are caught when v_2/v_1 exceeds 1.28; while to make water condense on any of the positive ions v_2/v_1 must exceed about 1.31; all the ions positive and negative being caught when v_2/v_1 exceeds 1.35.

Experiments were now made in which the expansion did not take place till after the rays had been cut off.

The ions which are being attracted from the ionised layer to the lower plate, have at the most about $3\frac{1}{2}$ millims. to travel, while the upward moving ones have from 17 to 20 millims. to travel. One would expect, therefore, about six times as long a time to be taken for the removal of the latter as is required for the removal of the former. There is thus a considerable range of time available for making the expansion, so that the majority of the ions of one kind shall still be present, while all the ions of the other kind have reached the lower plate. Using one LECLANCHÉ cell to maintain the electric field between the plates, an interval of about 1 second between cutting off the rays and making the expansion was found to be suitable.

The results were in agreement with those previously obtained; the drops, when the field was such as to give positive ions and v_2/v_1 was less than 1.31, were now no more numerous than if the expansion were made without exposure to the rays at all. The method, therefore, enables us to obtain ions entirely of one kind.

To test to what degree accidental variations in the time allowed to elapse between cutting off the rays and making the expansion could affect the result, some experiments were made in which this interval was varied. A metronome, giving 90 ticks per minute, was used; the interval before the expansion was varied by switching off the current from the coil, as the metronome made a tick, and pulling the trigger of the expansion apparatus at the moment of the first, second, or any subsequent tick thereafter. The following results were obtained, one LECLANCHÉ cell being used to maintain the field. The expansion was such as to catch negative ions only.

(1) NEGATIVE Ions moving upward.

v_2/v_1 .	Interval in seconds.	Result.
1.27	$\frac{2}{3}$	Dense fog
1.27	$1\frac{1}{3}$	Dense fog
1.27	2	Fog
1.27	$2\frac{2}{3}$	Slight fog
1.27	$3\frac{1}{3}$	Dense shower
1.27	4	Very few drops (no more than without rays)

The negative ions thus take between 3 and 4 seconds to travel from the ionised layer to the upper plate, and a large proportion of them are still present more than 2 seconds after turning off the rays. The field was now reversed.

(2) NEGATIVE Ions moving downwards.

$r_2 r_1$.	Interval in seconds.	Result.
1.27	$\frac{2}{3}$	Very few drops
1.30	$1\frac{1}{3}$	Very few drops (no more than without rays)

All the negative ions have now reached the lower plate in two-thirds of a second after turning off the rays. That the positive ions are still present was proved by increasing the expansion to 1.34 (which is sufficient to cause water to condense on them also); a fog was now obtained when the interval was $1\frac{1}{3}$ seconds. The actual time taken for the positive ions to disappear was not measured, but as ZELENY's experiments show that they move more slowly than the negative, they would doubtless have been found to take at least as long as the negative to travel to the upper plate.

The above results show that any accidental differences in the length of the time between cutting off the rays and making the expansion are of little importance when the interval amounts to about 1 second.

The time taken for the ions to be removed, when they have to travel to the upper plate, is somewhat longer than the time we obtain by calculation, using RUTHERFORD's* value for the velocity of the ions. The time calculated in this way amounts to about 2 seconds. The want of uniformity in the field is sufficient to account for the actual time being longer than the calculated.

The following tables contain the results of observations in which the expansion was effected about 1 second after cutting off the supply of Röntgen rays.

* 'Phil. Mag.,' vol. 44, p. 422, 1897

RAYS turned off before expansion. Difference of potential between plates,
1 Leclanché cell.

v_2/v_1 .	Result.	
	Upper plate negative (positive ions in excess).	Upper plate positive (negative ions in excess).
1.28	1 or 2 drops	Fog
1.29	1 or 2 drops	Fog
1.31	Very few drops	Fog
1.32	Drops few	Fog
1.33	Shower	Fog
1.34	Slight fog	Fog
1.36	Fog as dense as negative fogs	Fog

The effect of the positive ions begins to be detected when v_2/v_1 amounts to about 1.32 or 1.33; below that point no more drops are seen than in the absence of the rays.

The next series shows the point at which the positive ions first begin to be detected more sharply defined.

RAYS turned off before expansion. Difference of potential between the plates,
1 Leclanché cell.

v_2/v_1	Result.	
	Upper plate negative (positive ions in excess).	Upper plate positive (negative ions in excess).
1.265	1 or 2 drops	Fog
1.31	1 or 2 drops	Fog
1.32	Slight fog	Fog
1.35	Fog as dense as negative	Fog

Positive ions begin to be caught when v_2/v_1 is between 1.31 and 1.32.

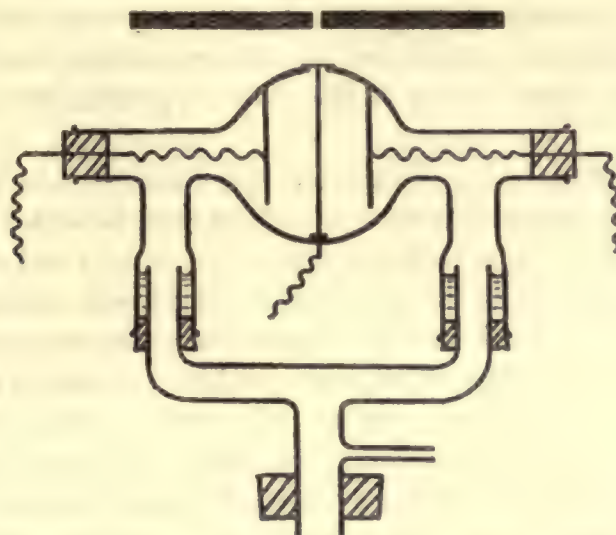
A double apparatus was now constructed, to allow of the comparison of fogs produced simultaneously in the presence of positive and negative ions respectively.

The arrangements for causing the sudden expansion were the same as before. The general form of the rest of the apparatus is indicated in the diagram (fig. 2) which is drawn approximately to scale.

The vessel in which the clouds were observed was nearly spherical, and about 5.8 centims. in diameter. It was divided into two equal chambers by a partition of brass (about 1 millim. thick) in the equatorial plane; the vessel was cut in two to allow of its insertion, the edges of the two halves being ground smooth, to allow

them to be easily cemented against the faces of the partition. The latter was circular, its diameter being equal to the outside diameter of the vessel. A narrow strip of brass, $2\frac{1}{2}$ millims. in thickness, was soldered to each face, extending all round the circumference, except for a gap of 4.5 centims. at the top. When the ground edges of the two halves of the vessel were cemented against these strips there was left at the top a slit on each side of the brass plate, 4.5 centims. long and 2.5 millims. wide. The double slit was closed by covering it with a strip of thin aluminium cemented to the outer surface of the glass and to the edge of the brass partition. A thin layer of air in contact with each surface could thus be exposed to the Röntgen rays from a source placed vertically above the partition.

Fig 2.



Each half of the apparatus contained a second brass plate fixed parallel to the central plate at a distance of 1.8 centim. from it. These had the form of equilateral triangles, and were fixed to the glass with sealing wax at the corners. There was room between the sides of the triangle and the walls of the vessel for the air to escape from between the plates at the moment of expansion.

The metal plates were, as in the former apparatus, covered with wet filter paper.

The anticathode of the focus tube, which generated the rays, was fixed by eye vertically above the central plate of the apparatus. A lead screen connected to earth and provided with a slit, 4 millims. in width, was placed about 2 centims. above the aluminium window of the cloud vessel. The final adjustments were made by moving the screen until, when both side plates were kept at the same potential (higher than that of the central plate, which was always earthed), exactly equal fogs were obtained on the two sides, with expansions sufficient to catch the negative ions.

To make the fogs on the two sides readily visible simultaneously, a horizontal stratum of the air in both halves was illuminated by the light from a horizontally placed luminous gas flame brought to a focus within the apparatus, the source being behind

the apparatus with its centre in the plane of the central plate. The fogs were best seen when the eye was placed sufficiently below the level of the illuminated stratum to receive none of the direct light, but only that scattered by the drops.

To compare the effects of positive and negative ions, expansions were made with the left-hand plate at a certain positive potential (generally about 1 volt), the right-hand plate being at an equal negative potential and the central plate earthed. The appearance of the fogs on the two sides was noted, the direction of the fields reversed, and the effect of an expansion of the same amount as before again noted. Any effect due to want of symmetry in the apparatus was thus eliminated.

To secure equality in the electric fields in the two halves of the apparatus, the following arrangement was used. The source of potential (generally two Leclanché cells in series) had its terminals connected by a resistance of 200 ohms. The middle point of this resistance was earthed, and the two extremities were connected through a commutator to the outer plates of the cloud apparatus, the central plate being earthed.

The correction to be applied to obtain the true values of v_2/v_1 was found to be the same as before; to the apparent values of $v_2/v_1 \cdot 03$ must be added. The error was, as before, found to be the same at both the points, $v_2/v_1 = 1.25$ and $v_2/v_1 = 1.38$.

To obtain an approximation to quantitative comparison between the number of drops produced in the two halves of the apparatus, measurements were made on the time taken by the upper surface of the clouds on the two sides to sink below the level of the beam of light, which was used to make them visible. The expansion and consequent cooling on both sides being the same, the same quantity of water is condensed in each half; the quantity available for each drop is thus inversely proportional to the number of drops which are formed. Now the radii of the drops on the two sides can be compared by measuring the velocity with which they fall; a comparison of the rates of fall on the two sides will thus enable us to determine the ratio between the numbers of the drops produced in the two halves of the apparatus, or will at least serve as a test for equality between the numbers. Professor J. J. THOMSON* has in fact used the rate of fall of the drops, formed on the ions as the result of expansion, to determine the number of the ions present, from which he obtains an estimate of the charge carried by each.

The results of measurements with this double apparatus are given in the tables which follow. After what has already been said in connection with the other apparatus, it is hardly necessary to point out that, when the right-hand plate is connected to the positive terminal of the battery, and the left-hand plate to the negative terminal (the central plate being at zero potential), there will be a great excess of negative ions on the right, and of positive ions on the left. The terms "positive" and "negative" in the tables refer to the sign of the charge carried by the majority of the ions, not to the potentials of the plates; the corrected values of v_2/v_1 are given.

* 'Phil. Mag.,' *loc. cit.*

FIELDS produced by 4 Leclanché cells, terminals joined by resistance of 200 ohms, the middle point of which was earthed.

v_2/v_1 .	Time taken by fogs to fall in seconds.		Ratio of times, negative / positive.
	Left side.	Right side.	
1.28	positive 5 negative 15	negative 16 positive 3	$\left. \begin{matrix} 3.2 \\ 5.0 \end{matrix} \right\} 4.1$
1.30	negative 15 positive 5 negative 10 positive 2	positive 2 negative 15 positive 2 negative 10	$\left. \begin{matrix} 7.5 \\ 3.0 \\ 5.0 \\ 5.0 \end{matrix} \right\} 5.1$
1.31	positive 7 negative 14	negative 12 positive 7	$\left. \begin{matrix} 1.7 \\ 2.0 \end{matrix} \right\} 1.8$
1.32	negative 8 positive 8 negative 14 positive 12	positive 5 negative 10 positive 8 negative 17	$\left. \begin{matrix} 1.6 \\ 1.2 \\ 1.7 \\ 1.4 \end{matrix} \right\} 1.5$
1.33	negative 12 positive 12	positive 10 negative 13	$\left. \begin{matrix} 1.2 \\ 1.1 \end{matrix} \right\} 1.15$
1.35	negative 10 positive 10	positive 10 negative 10	$\left. \begin{matrix} 1.0 \\ 1.0 \end{matrix} \right\} 1.0$

The results of another series, in which only two cells were used to produce the fields, are given in the next table.

v_2/v_1 .	Time taken by fogs to fall in seconds.		Ratio of times, negative / positive.
	Left side.	Right side.	
1.28	positive 4 negative 14	negative 15 positive 4	$\left. \begin{matrix} 3.7 \\ 3.5 \end{matrix} \right\} 3.6$
1.30	negative 14 positive 3	positive 4 negative 17	$\left. \begin{matrix} 3.5 \\ 5.7 \end{matrix} \right\} 4.6$
1.32	positive 10 negative 20	negative 17 positive 12	$\left. \begin{matrix} 1.7 \\ 1.7 \end{matrix} \right\} 1.7$
1.34	negative 20 positive 12	positive 17 negative 17	$\left. \begin{matrix} 1.2 \\ 1.4 \end{matrix} \right\} 1.3$
1.36	negative 20 positive 20	positive 20 negative 20	$\left. \begin{matrix} 1.0 \\ 1.0 \end{matrix} \right\} 1.0$
1.37	positive 18 negative 20	negative 18 positive 20	$\left. \begin{matrix} 1.0 \\ 1.0 \end{matrix} \right\} 1.0$

The tables show plainly that with the smaller expansions the number of drops on the side which contains chiefly positive ions is very small compared with the number of drops on the side containing mainly negative ions. No difference can be detected between the fogs on the two sides when v_2/v_1 exceeds 1.35; the transition from the one kind of result to the other begins when v_2/v_1 is about 1.31. This is well shown by the ratio of the times taken by the fogs on the negative and positive sides to fall the same distance; increasing v_2/v_1 from 1.30 to 1.31 brings down the ratio from 5.1 to 1.8 in the first series, and in the second series the ratio diminishes from 4.6 to 1.7 as v_2/v_1 is increased from 1.30 to 1.32. The results are therefore in complete agreement with those previously obtained.

There can be no doubt that the drops which are formed when v_2/v_1 is less than 1.31 on the side containing mainly positive ions are deposited on negative ions, of which a considerable number must unavoidably be present, when the expansion is made while the rays are acting. The number of these was exceedingly small when the rays were turned off before the expansion was made.

There is no evidence of any increase in the number of the negative ions caught as v_2/v_1 passes through the region in which the positive ions begin to be caught. The following is an example of observations with expansions of different amount made in rapid succession (so that the radiation might not have time to change in intensity):—

v_2/v_1	Time taken by fogs to fall.	
	Left side.	Right side.
1.30	positive 2 seconds	negative 12 seconds
1.30	negative 12 "	positive 3 "
1.37	negative 12 "	positive 12 "
1.37	positive 12 "	negative 12 "

The rate of fall on the negative side is the same when $v_2/v_1 = 1.37$ as when it = 1.30. It is true that we would expect the drops if equally numerous to fall slightly quicker with the greater expansion, since a rather larger quantity of water would be condensed; against this is to be set the fact that the positive minority on the negative side are caught by means of the greater expansion, and not by the less.

It will be convenient to consider here what light the new knowledge now acquired throws upon phenomena previously observed in the course of experiments with expansion apparatus.

All the former measurements which I have published upon the least expansion required to make condensation take place in presence of ions, are now seen to have been concerned with negative ions only. One example of interest is the case of nuclei produced by a zinc plate exposed to ultra-violet light. When the plate was negatively charged, nuclei were found to be present, requiring an expansion, $v_2/v_1 = 1.25$, to make

water condense on them; a fact in agreement with the results of the present investigation, since negative ions were, in this case, plainly in question. The absence of fog when the expansion was made with the field reversed was, however, as we now see, no proof that no ions escape from the positively charged plate, for the expansions used were insufficient to cause water to condense on positive ions had they been present. Another case of interest is that of the nuclei produced by the discharge from a point. Even when positive electricity was escaping from the point, fogs were obtained with expansions which are now seen to have been insufficient to catch positive ions. We are therefore driven to the conclusion that the positive discharge does not consist simply in the escape of positive ions from the point of the wire, but that negative ions (or nuclei of some other kind than ions) are present as well, possibly produced by the action upon the moist air of the radiation from the glowing point of the wire.

Indications had already been noticed of an increase in the number of drops, produced in ionised air as v_2/v_1 was increased beyond the point now shown to be that at which the positive ions first begin to act as condensation nuclei. Professor THOMSON was indeed led to make the suggestion contained in the words quoted at the beginning of this paper by noticing indications of such an increase in the neighbourhood of the point $v_2/v_1 = 1.3$. My own observations had also previously led me to believe that there was an increase at the point $v_2/v_1 = 1.31$; for example, my notes for March 4, 1898, contain the remark, "Many experiments with air, as well as H, seem to show that there are nuclei requiring expansion = 1.31 to catch them in addition to those appearing at 1.25."

Positive and negative ions (at least those produced in air by Röntgen rays) have now been proved to differ in their efficiency as condensation nuclei; they also differ, as ZELENY has shown, in the velocity with which they move in an electric field of given strength. The negative ions move the faster and are the more efficient as nuclei for the condensation of water vapour.

A possible way of accounting for both differences is to suppose that the charge carried by the negative ions is greater than that carried by the positive, the number of the latter being, of course, correspondingly greater. We might, for example, take the view that the ionisation consists in the breaking-up of the neutral molecules into a certain number of positive ions and half as many negative ions, each carrying twice as large a charge as the positive, a process which we can readily imagine to take place in the case of water molecules.

The experiments already described make this view hardly tenable, for we have seen that when the expansion is sufficient to make water condense on all the ions ($v_2/v_1 = 1.35$ or more) the fogs in the two halves of the apparatus are indistinguishable in appearance and in the rate of fall of the drops. We have still to consider to what extent this proves equality in the number of positive and negative ions produced.

The velocity with which the drops fall is proportional to the square of the radius,

that is, to the two-thirds power of the volume of each drop, or for a given expansion to $1/n^{2/3}$ where n is the number per cubic centimetre. The time, t , taken to fall a given distance is thus proportional to $n^{2/3}$, or the number of drops is proportional to $t^{3/2}$. Now, when v_2/v_1 exceeds 1.35 the times taken by the drops on the two sides to fall a given distance certainly do not differ by as much as 1 part in 10. If $t_1/t_2 = 1.1$ then $n_1/n_2 = 1.1^{3/2} = 1.15$. Thus the number of ions is the same on the two sides to within 15 per cent.

The equality of the fogs on the two sides is, in fact, rather more exact than we would expect; for the positive ions, according to ZELENY, take 1.25 times as long as the negative to travel a given distance. We would expect then (the strength of the field on each side being the same) that, if equal numbers of positive and negative ions were produced in a given time, the negative ions would be more quickly removed, and a somewhat larger number of drops should have been produced in the half containing mainly positive ions.

The absence of any indication of this slight excess of positive ions is of the less consequence for the present purpose, since it strengthens rather than weakens the evidence against the view that a larger number of positive than of negative ions is produced. As a test of the trustworthiness of the method for detecting a difference in the number of drops produced on the two sides, experiments were made in which the direction of the field on both sides of the central plate was such as to drive negative ions outwards towards the side plates; the strength of the field being, however, different on the two sides. The ratio of the fields was as 3 to 2, the stronger field being produced by two Leclanché cells. The following results were obtained:—

$v_2/v_1 = 1.30.$		
	Left side.	Right side.
Relative strength of fields . .	3	2
Time taken to fall	10 seconds	12 seconds
Relative strength of fields . .	2	3
Time taken to fall	12 seconds	10 seconds

The excess in the number of drops on the side of the weaker field is plainly shown.

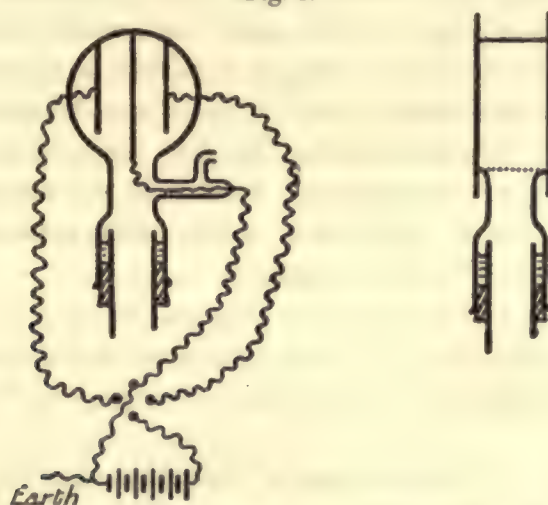
It appears, therefore, that the difference in the behaviour of the positive and negative ions is not to be explained by a difference in the quantity of electricity carried by positively and negatively charged ions respectively.

Some experiments were now tried with the object of determining whether the rain-like condensation, which takes place in dust-free air, even when not exposed to any ionising agents, is due to ions.

As already pointed out, the least expansion necessary to produce such showers in air initially saturated is identical with that required to cause condensation on ions—really on negative ions, as the experiments described in this paper show. This is a remarkable coincidence if we are really concerned with nuclei of entirely different kinds. Further, it was during experiments made in the absence of ionising agents that I first noticed indications of an increase in the number of the drops about the point $v_2/v_1 = 1.31$, the expansion now proved to be that required to cause water to condense on positive ions.

These considerations seemed to furnish strong ground for believing that the very few nuclei always present actually are ions. In a recent paper,* it is true, I described some unsuccessful attempts which I had made to remove the nuclei by applying a strong electric field; I did not, however, consider these experiments to be conclusive evidence against the ionic nature of the nuclei. I have, therefore, recently subjected them to a much more severe test by means of a differential apparatus (fig. 3).

Fig. 3.



The mechanism for causing the sudden expansion was the same as in the other experiments, and is not shown in the figure. A front view of the apparatus is given on the left, a side view on the right. It consists of a short glass cylinder, 4 centims. in diameter and 2 centims. long, the ends being ground smooth and closed by plates, that forming the front face being of glass, the other of quartz. (The quartz was for experiments with ultra-violet light described below.) A thin brass plate, 2 centims. wide (reaching, therefore, from back to front of the apparatus), divided the vessel into two equal chambers. On each side of this, at a distance of 8 millims., was a parallel brass plate of the same width, 2 centims., but not reaching to the lower wall of the cylinder. The brass plates were covered with wet filter paper.

A difference of potential of 320 volts could be maintained, by means of a series of

* 'Phil. Trans.,' A, vol. 192, pp. 403-453, 1899.

secondary cells, between the central plate and one of the side plates, the other being connected to the central plate, which was earthed. In one half, therefore, there was a strong electric field, in the other half, none. A lens was used to examine simultaneously the drops formed on the two sides of the central plate. Any difference in the number of the drops could thus readily be detected.

In the strong field the maximum length of life of an ion will be the time taken to travel from one plate to the other under the action of the field; in the present case, a distance of 8 millims., with a potential gradient of 320 volts in 8 millims., or 400 volts per centimetre. The velocity of the ions produced by X rays would in such a field be about 400×1.6 centim. per second, if we take RUTHERFORD'S value of the velocity for a potential gradient of 1 volt per centimetre. The 8 millims. would therefore be traversed in $.8/(400 \times 1.6) = 1/800$ of a second. (The time would really be somewhat longer on account of the plates being too small to give a sufficiently uniform field.) Now the average length of life of the ions due to Röntgen rays when they are destroyed by recombination alone is of the order of 1 second.* The fewer the ions also the less rapid is the rate at which they recombine; we would, therefore, expect the average life of the very few nuclei with which we are now concerned, if they really are ions, to be at least as long as 1 second in the absence of any electric field. If then we have here simply a case of spontaneous ionisation due to molecular encounters, we ought to obtain something like 800 times as many drops without the field as with it. In similar experiments† made with the ions produced by Röntgen or uranium rays, much weaker fields were in fact found sufficient to prevent almost completely the production of fogs by expansion.

In the experiments now made without external ionising agents, not the slightest difference could be detected between the appearance of the showers on the two sides of the apparatus. All degrees of expansion from $v_2/v_1 = 1.25$ to $v_2/v_1 = 1.38$ were tried.

If then we have here to do with a case of ionisation, it differs completely from the ionisation produced by Röntgen rays.

Very similar nuclei, requiring practically the same supersaturation to make water condense on them as the ions, are produced by the action on moist air of sunlight and of weak ultra-violet light. Former experiments‡ showed that the nuclei produced by this volume effect of ultra-violet light (unlike those produced by its action on a negatively charged zinc plate) are unaffected by electric fields strong enough to remove the ions produced by Röntgen rays as fast as they are produced. More severe tests were now made with the double apparatus, to see whether they are altogether uninfluenced by the electric field.

The ultra-violet light was produced by the spark discharge between aluminium

* RUTHERFORD, *loc. cit.*

† 'Phil. Trans.,' A, vol. 192, pp. 403-453, 1899. Also J. J. THOMSON, 'Phil. Mag.,' *loc. cit.*

‡ 'Phil. Trans.,' *loc. cit.*

terminals, at a distance of 55 centims. from the quartz plate in one series of experiments, at 180 centims. in another. In neither case was the radiation strong enough to cause drops to be produced with expansions appreciably below $v_2/v_1 = 1.25$. The spark-terminals were placed in the plane of the central plate, so that the air in both halves was equally exposed to the rays. The wet filter paper which covered the brass plates prevented any surface effect from the light which might reach the plates. As before, the air on one side was between plates at the same potential, that on the other side in a strong field. The central plate was earthed and one of the side plates kept at a positive potential of 320 volts, the other being earthed; the connections were interchanged after each observation, so that the air in each half alternately was subjected to the action of the field.

When the expansions were made while the air was exposed to the rays, no difference could be detected between the fogs in the two halves of the apparatus. Moreover, even when the rays were turned off 10 seconds before the expansion was made, a slight fog was obtained, equally dense on both sides of the central plate. Thus some of the nuclei appear to persist for 10 seconds, and even in that time the field has had no sensible effect in reducing the number of the nuclei.

A field, therefore, of 400 volts per centimetre causes the nuclei to move in 10 seconds, a distance small compared with 8 millims., the distance between the plates. This gives, for the velocity under a potential gradient of 1 volt per centimetre, less than $1/4000$ centim. per second, whereas the ions produced by Röntgen rays travel under these conditions between 1 and 2 centims. per second.

The slight rain-like condensation which takes place, when v_2/v_1 lies between 1.25 and 1.38, in the absence of all radiation, as well as the much denser condensation produced by the same expansions when the air is exposed to weak ultra-violet light, are thus essentially different phenomena from the apparently similar condensation produced in air ionised by Röntgen rays.

We might perhaps most naturally conclude that we are in these cases not concerned with ions at all. There is, however, the difficulty of the unlikelihood of two entirely different classes of nuclei being so exactly identical in the degree of supersaturation necessary to cause water to condense on them. The apparent existence of a second coincidence (an increase of the number of drops when v_2/v_1 exceeds 1.31) is still harder to explain on this view.

It is possible that condensation in these cases really does take place on ions carrying the same charge as those produced by Röntgen rays. There are, in fact, several ways in which we may account for the fact that an electric field does not remove them.

We might suppose that the nuclei differ from those produced by Röntgen rays merely in being so much larger, that their velocity in a given field is diminished enormously, the charge in each nucleus remaining the same. It is difficult, however, to believe that the efficiency of the nucleus in helping condensation would remain

unaltered by such an increase in size as would reduce the velocity to anything like such a small value as $1/4000$ centim. per second for a potential gradient of 1 volt per centimetre. In fact, if we can trust to obtaining approximately correct results by applying to drops as small as 2×10^{-6} centim., the formulæ which hold for larger drops, we can see* that these nuclei must amount to at least 2×10^{-6} centim. in radius; the supersaturation required to cause condensation to take place on drops of this radius being that produced by an expansion, $v_2/v_1 =$ about 1.01, which is very far removed from that actually required, $v_2/v_1 = 1.25$.

The ionisation may be a result of the expansion. This is the view I am inclined to take.

It is easy to understand, according to this view, how the number of drops produced is entirely uninfluenced by even a strong electric field, for the whole time for which the ions would be free to move under the action of the field, before the formation of drops upon them, would be exceedingly short.

Uncharged nuclei are probably present before the expansion. Some change is produced in the air by weak ultra-violet light independently of the expansion, for, as we have seen, the fogs may be obtained even when the expansion is made some seconds after the light has been cut off. The behaviour of moist air exposed to stronger ultra-violet light, and especially the extreme case where we get visible particles produced without expansion, almost compel us to conclude that even weak ultra-violet light produces nuclei before the expansion is made. I have already suggested† that these nuclei consist of what we may regard as minute water drops containing hydrogen peroxide in solution. The difference between the effects of the strongest and weakest ultra-violet light would consist in a difference in the size of these drops due to the larger quantity of hydrogen peroxide produced in each by the stronger radiation. We may suppose the very minute molecular aggregates due to weak ultra-violet light to be of themselves too small to act directly as condensation nuclei with the expansion $v_2/v_1 = 1.25$; in other words, the growth which results from the supersaturation corresponding to this expansion may be insufficient to bring them up to the critical size beyond which the unstable condition is reached, where increase in size is accompanied by a diminution of the equilibrium vapour pressure. But if, as a consequence of the increase in size which results from the supersaturation, the nucleus becomes charged, an ion carrying electricity of opposite sign to that left on the original nucleus being thrown off, the result actually met with would be explained. Judging from the behaviour of hydrogen peroxide solutions, with respect to the electricity developed by splashing, we would expect the original nucleus to become negatively charged; for the splashing results in a negative electrification of the drops‡ indicating that the inner coat of the double layer originally covering the

* Using the value found by Professor THOMSON (*loc. cit.*) for the charge on one ion, and applying the formula for the steady motion of a sphere through a viscous fluid (LAMB, 'Hydrodynamics,' p. 532).

† 'Phil. Trans.,' *loc. cit.*

‡ J. J. THOMSON, 'Phil. Mag.,' vol. 37, p. 341, 1894.

drops is negative; in other words, that solutions of hydrogen peroxide in water, surrounded by air, attract negative electricity more than positive.

The view here suggested is, therefore, that the nuclei requiring the definite expansions 1.25 or 1.31 to make water condense on them are always really ions, the cases in which an electric field is without influence upon the result of expansion being explained by supposing that the ionisation does not in such cases take place until supersaturation is produced.

The separation of the positive and negative electricity by the formation of drops on the negative ions only, as soon as the supersaturated state reaches the necessary limit, will take place equally well whether the ions exist before the supersaturation is produced or are the result of the supersaturation. Moreover, if the initial growth of a drop, as above suggested, is able to cause it to acquire a charge equal to that of one ion, the further growth of the drop may result in an increase of the charge. The drops may thus acquire a charge considerably exceeding that of one ion, even if there be no coalescence of small drops to form large ones.

Further experiments on this point are evidently required.

I do not propose to discuss here the meteorological bearings of the results obtained. The questions with which the experiments are concerned are, I think, fundamental ones in connection with the electrical effects of precipitation. From this point of view the principal results of this investigation are:—

(1.) To cause water to condense on negatively charged ions, the supersaturation must reach the limit corresponding to the expansion $v_2/v_1 = 1.25$ (approximately a fourfold supersaturation). To make water condense on positively charged ions, the supersaturation must reach the much higher limit corresponding to the expansion $v_2/v_1 = 1.31$ (the supersaturation being then nearly sixfold).

(2.) The nuclei, of which a very small number can always be detected by expansion experiments with air in the absence of external ionising agents, and which require exactly the same supersaturation as ions to make water condense on them (as well as the similar nuclei produced in much greater numbers by the action of weak ultra-violet light on moist air) cannot be regarded as free ions, unless we suppose the ionisation to be developed by the process of producing the supersaturation.

We see, then, that if ions ever act as condensation nuclei in the atmosphere, it must be mainly or solely the negative ones which do so, and thus a preponderance of negative electricity will be carried down by precipitation to the earth's surface.

The experiments described in this paper were carried out at the Cavendish Laboratory.

NOTE ADDED SEPTEMBER 25, 1899.

In order that the results of these investigations should have a direct bearing on the subject of atmospheric electricity, it is necessary to assume that condensation in the atmosphere frequently takes place from the supersaturated condition. There is

very little direct evidence of the existence of supersaturation in the atmosphere, but there is at least an equal lack of evidence against its existence above the lower cloud layers even as a normal accompaniment of precipitation. That supersaturation occurs in connection with thunderstorms is held by v. BEZOLD and others ('Sitzungsb. Akad. d. Wissenschaft. zu Berlin,' 1892).

In the lower dust-charged layers of the atmosphere supersaturation is not to be expected. When there is an ascending air current, however, the dust particles may be retained in the lower cloud layers, through each becoming loaded with water, and ceasing to rise as soon as a certain critical size, depending on the upward velocity of the air, is attained. Supersaturation will exist under these conditions in the air which has left its dust particles behind, and if the ascending current reaches a sufficient elevation a second condensation will take place at a higher level, as was pointed out in a former paper ('Phil. Trans.,' A, vol. 189, p. 286, 1897); the conditions will then be such that the experimental results obtained in the present investigation may be applied.

Whether the drops will from the first be too large to be supported by the upward current and therefore at once begin to fall as raindrops, growing rapidly as they fall through the supersaturated layers, or will still continue to be supported by the ascending current and form an upper cloud layer, depends on the upward velocity of the air, the number of nuclei (negative ions?) and other conditions. In either case we should expect the drops to be negatively charged, the air rising above them carrying a corresponding excess of positive ions.

X. On the Resistance to Torsion of Certain Forms of Shafting, with Special Reference to the Effect of Keyways.

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Communicated by Professor M. J. M. HILL, F.R.S.

Received June 1,—Read June 15, 1899.

§ 1. *Object and Methods of the Investigation.*

THE object of the present paper is to obtain solutions of the problem of torsion for cylinders whose cross-sections are bounded by confocal conics. It is mainly an extension of DE SAINT-VENANT's investigations, and is based upon his general equations of torsion.

The method employed depends upon the use of conjugate functions ξ and η , such that $\xi = \text{const.}$ represents confocal ellipses and $\eta = \text{const.}$ confocal hyperbolas.

The use of conjugate functions for the torsion problem has been suggested by THOMSON and TAIT ('Natural Philosophy'), by CLEBSCH ('Theorie der Elasticität fester Körper,' §§ 33–35), and by BOUSSINESQ ('Journal de Mathématiques,' pp. 177–186, Série III., vol. 6). CLEBSCH has used such elliptic coordinates to solve the torsion problem for hollow cylinders bounded by confocal ellipses, and DE SAINT-VENANT has applied conjugate functions to the same problem for shafts whose sections are sectors of circles; curvilinear coordinates have also been employed by Mr. H. M. MACDONALD ("On the Torsional Strength of Hollow Shafts," 'Proc. Camb. Phil. Soc.,' vol. 8, 1893, p. 62, *et seq.*), but I am not aware that the actual solution has yet been obtained for sections bounded by both ellipses and hyperbolas.

The work proceeds on lines analogous to those developed by SAINT-VENANT himself, in his solution of the problem of torsion for the cylinder of rectangular cross-section. The strains and stresses are expressible in terms of infinite series involving circular and hyperbolic functions.

The boundaries of the section are given by constant values of ξ and η . The values of ξ are taken to be $\pm \alpha$.

The conditions from which the unknown quantity w (the shift parallel to the axis) is determined are

$$d^2w/dx^2 + d^2w/dy^2 = 0$$

throughout the section; and

$$dw/dn + (mx - ly)\tau = 0$$

along the boundary, where dn = an element of the outwards normal to the boundary, τ is the angle of torsion per unit length, and l, m are the direction-cosines of dn .

Now in the present case

$$dn = \pm d\xi \times (c\sqrt{J})$$

where

$$J = \partial \left(\frac{x}{c}, \frac{y}{c} \right) / \partial (\xi, \eta)$$

at the boundary where $\xi = \text{const.}$, and

$$dn = \pm d\eta \times (c\sqrt{J})$$

at the boundary where $\eta = \text{const.}$, the sign being so determined that dn is positive.

By adding suitable terms to w , we can reduce one or other of the boundary conditions to the form

$$dw_1/dn = 0,$$

where

$$w = w_1 + \text{suitable terms.}$$

Suppose we make

$$\left(\frac{dw_1}{d\xi} \right)_{\xi=\pm\alpha} = 0.$$

Expanding now w_1 in the form of a series,

$$w_1 = \sum_{n=0}^{n=\infty} A_n \sinh \left\{ \frac{2n+1}{2\alpha} \pi (\eta + \kappa) \right\} \sin \frac{2n+1}{2\alpha} \pi \xi,$$

the differential equation and the first boundary condition are identically satisfied.

When this value is substituted in the second boundary condition, we get an equation expressing a given function of ξ in a series of sines of odd multiples of $\frac{\pi\xi}{2\alpha}$, between the limits $+\alpha$ and $-\alpha$.

But such an expression can be definitely obtained by a method analogous to that for FOURIER'S series. Comparing coefficients, we obtain relations which determine completely all the constants in the expression of w_1 .

w is then known. The shears and torsion moment are then deduced by differentiation and a double integration.

§ 2. *Summary of the Results.*

The cross-sections which are dealt with in the present paper are of very great generality, and they include as special cases many of the cross-sections which SAINT-VENANT has worked out, for instance the rectangle and the sector of a circle.

The first section of which I treat is that bounded by an ellipse and two confocal

hyperbolas. Although the analysis is worked out for the case where the two hyperbolic segments are not symmetrical, I have not given any numerical examples of this case, as the sections obtained by taking two hyperbolas curved the same way, as in fig. 1, do not correspond to any intersecting practical case: the section is too broad at the ends and too narrow at the bend to be any fair representation of the angle iron.

The section (fig. 2) bounded by an ellipse and the two branches of a confocal hyperbola is, on the other hand, an approximate representation of a well-known section, much used in engineering practice, the rail section.

This section I have worked out for various values of the eccentricity of the ellipse and of the angle between the asymptotes of the hyperbola.

The four sections in fig. 2, where this angle is 120° , give the best representation of the rail section.

The numerical results are tabulated so as to show the ratio of the torsional rigidity of this section to that of the circular section of the same area, and also the same ratio for the maximum stress.

The ratio of these two ratios gives us a kind of measure of the usefulness or "efficiency" of the section.

In the case of the sections of fig. 2 I have investigated at length the position of the *fail-points*, or points of maximum strain and stress, the maximum strain, in the case of torsion, being coincident with the maximum stress. It is found that for the two smaller ellipses the maximum stress occurs at the point B where the section is thinnest. For the two larger ellipses the maximum stress occurs at points F, F, F, F, symmetrically distributed round the contour, and lying on the broad sides of the section. The critical section, when these two cases pass into one another, can be calculated and is shown as *qq*, *qq* in fig. 2. In figs. 2-5 the corresponding points belonging to the different sections are distinguished by suffixes.

The changes in the stresses are shown by the curves in fig. 9, (p. 340) in which the abscissa represents the quantity α whose hyperbolic cosine and sine are proportional to the major and minor axes of the ellipse respectively, and in which the ordinates represent the stresses at A, B, F, divided by the maximum stress of the circular section of equal area. The curves are in certain parts only roughly drawn, but they suffice to show the manner in which the stresses vary. It is seen that the stress at B separates from the maximum stress after the critical value $\alpha = 1.225$, and gradually diminishes, compared with the stresses at A and F.

This result might have been expected from the investigations of DE SAINT-VENANT upon certain sections bounded by curves of the fourth degree. These investigations appear, however, not to have been sufficiently noticed. THOMSON and TAIT, in their 'Natural Philosophy,' and BOUSSINESQ, in his researches on torsion ('Journal de Mathématiques,' Série II., vol. 16, p. 200), both conclude that the fail-points are at the points of the cross-section nearest to the centre, and BOUSSINESQ even gives an

apparently general proof of this proposition. His proof, however, is subject to certain restrictions which I point out, and which prevent it from being applied to the sections I am dealing with.

The sections are sensibly less useful than the circular section, their torsional rigidity

Fig. 1.

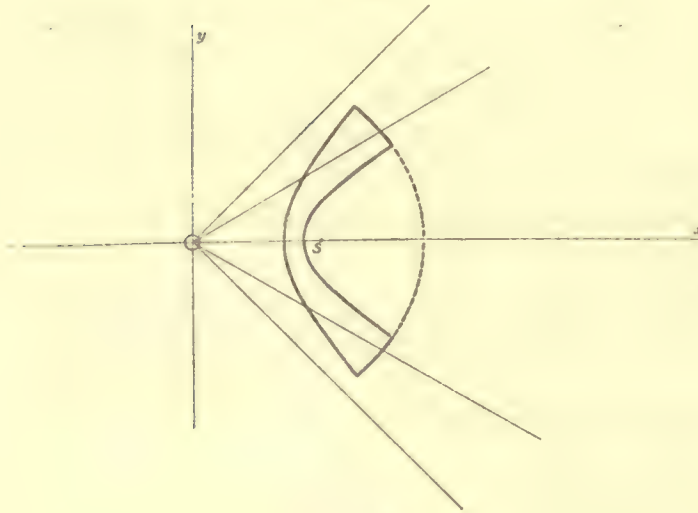


Fig. 3.

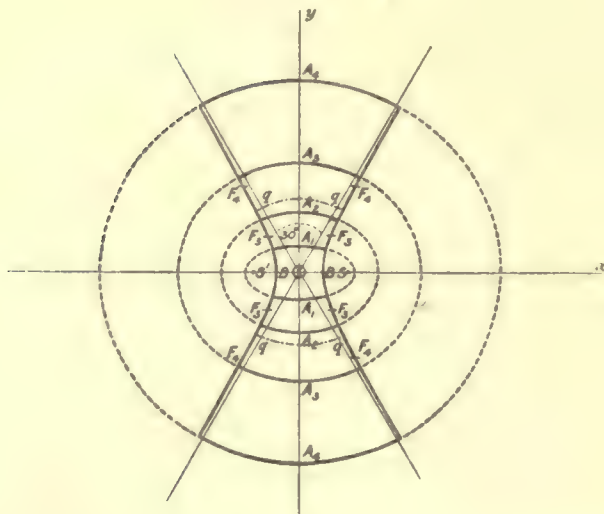
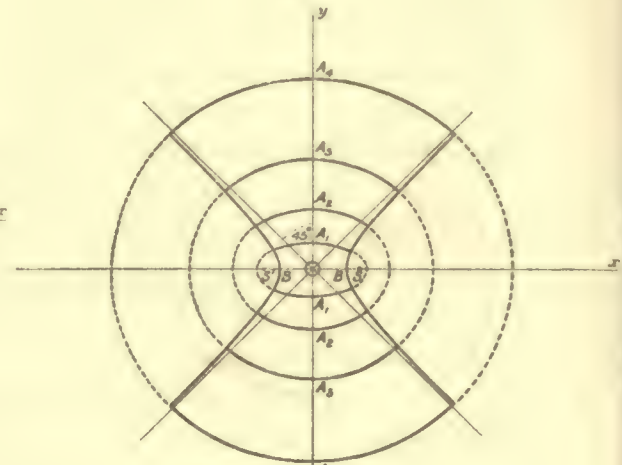


Fig. 2.

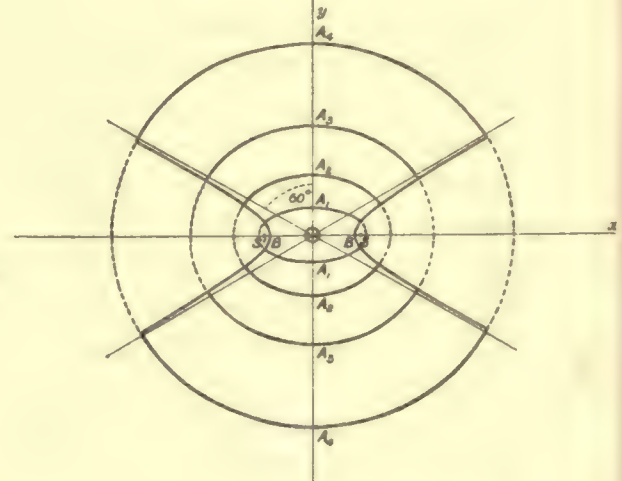


Fig. 4.

being always diminished and the maximum stress very often increased. This remark, I may add, applies to all the sections dealt with in this paper.

This usefulness or efficiency decreases as the neck of the section becomes more narrow, as, indeed, might have been anticipated.

Other sections worked out are those corresponding to angles between the asymptotes of 90° (fig. 3), 60° (fig. 4), and 0° (fig. 5); in the latter case the sections degenerate into ordinary elliptic sections with two straight slits, or indefinitely thin

keyways, cut into them along the major axis, as far as the foci. The stress at the foci, however, is then theoretically infinite.

It is interesting to see how, as we make the bend round the foci sharper, the values of α , for which the two fail-points break up into four, become larger and larger,

Fig. 5.

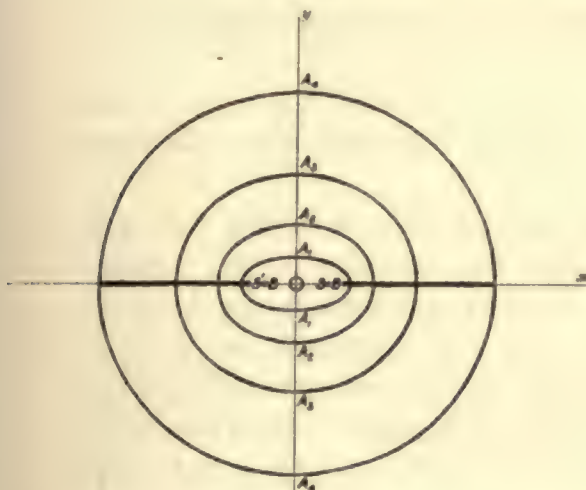


Fig. 7.

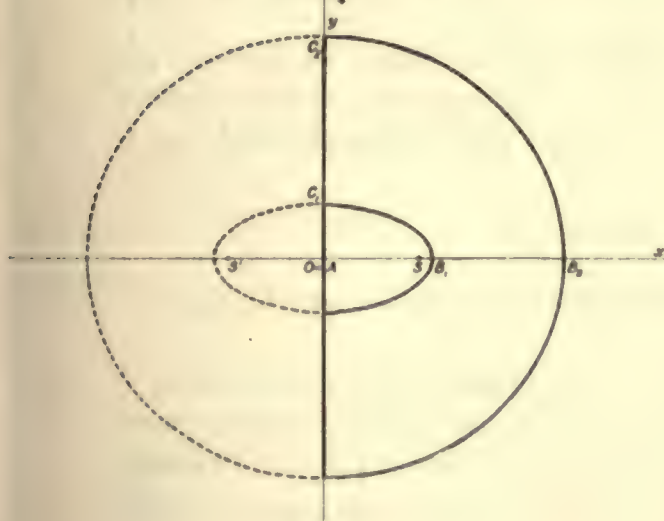
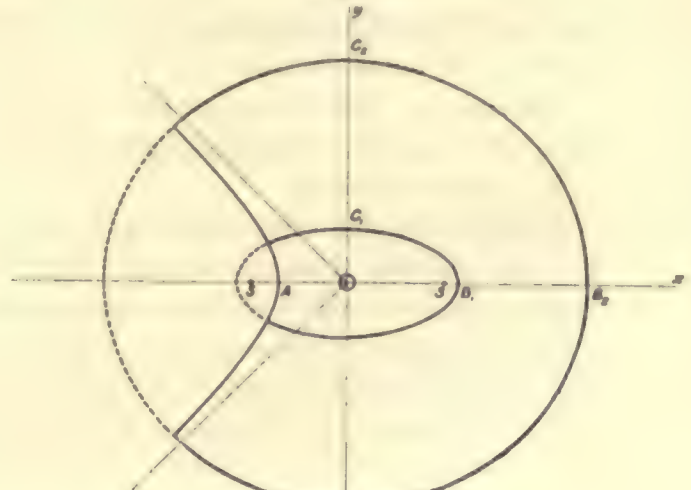


Fig. 6.

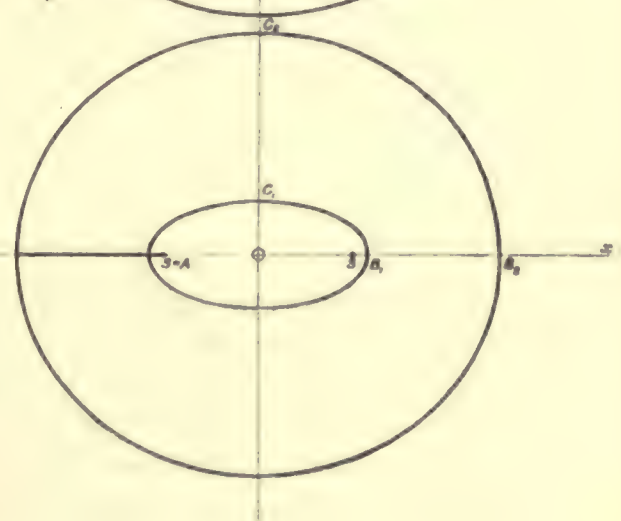


Fig. 8.

until, when the angle between the asymptotes of the hyperbolas is less than 73° , the greatest stress always occurs at the neck of the section.

The limiting case of such sections, when the angle between the asymptotes is very small and the eccentricity of the ellipse nearly unity, the distance between the foci being very great, gives us the rectangle.

I then pass on to the section bounded by one ellipse and one confocal hyperbola. In the limiting case when the foci coincide, we obtain the sector of a circle.

Of this I have worked out numerically three cases, in each case taking two ellipses

- (1.) The semi-ellipse (fig. 6).
- (2.) The ellipse with a keyway cut into it of the shape of a rectangular confocal hyperbola (fig. 7).
- (3.) The ellipse with a single slit cut into it (fig. 8).

The most striking of the results is in reference to the reduction of the torsional rigidity of the ellipse in case (3). This reduction of rigidity decreases rapidly as the depth of the notch decreases.

The rigidity, which is reduced by as much as 23 per cent. when the depth of the keyway is as great as $\cdot 6$ (semi-major axis), falls only about 1 per cent. when this depth is $\cdot 12$ (semi-major axis).

Possibly this may throw some light on the fact that the effect of cutting such slits into the material does not always give in practice the reduction in the torsional rigidity which should have been expected from SAINT-VENANT'S results for the circle. Clearly the depth of the keyway is a factor of the very first importance, and keyways of moderate depth will produce a comparatively small effect on the torsional rigidity.

It is also shown that the effect of cutting two equal and opposite slits is practically equal, in the two cases which I have calculated (namely, $\alpha = \pi/6$ and $\alpha = \pi/2$), to twice the effect of a single slit.

It seems, therefore, that the study of these sections brings to light several interesting facts in the theory of elasticity, and will well repay the trouble involved in dealing with the long and somewhat tedious algebra and arithmetic which lead to these results.

§ 3. *Statement of Notation, &c.*

In what follows the axis of z will be taken parallel to the generators, the axes of x and y in one of the terminal cross-sections.

The origin, however, will not necessarily be at the centroid of the cross-section.

The shifts of any point of the material parallel to the axis will be denoted as usual by u, v, w , and for the stresses I shall use the notation of TODHUNTER and PEARSON'S 'History of Elasticity,' \widehat{rs} denoting the stress, parallel to r , across a plane element perpendicular to s .

Then if, following SAINT-VENANT, we suppose the terminal cross-section $z = 0$ to be fixed (that is to say, $u = 0, v = 0$, but $w \neq 0$), then if τ be the angle of torsion per unit length,

$$v = \tau xz, \quad u = -\tau yz \quad \dots \dots \dots (1).$$

If μ be the modulus of rigidity,

$$\frac{\widehat{yz}}{\mu} = \frac{dw}{dy} + \tau x, \quad \frac{\widehat{xz}}{\mu} = \frac{dw}{dx} - \tau y \quad \dots \dots \dots (2),$$

and all the other stresses are zero.

w is then determined from the body stress equation

$$\frac{d\widehat{xz}}{dx} + \frac{d\widehat{yz}}{dy} = 0,$$

(11)

[illegible]

which holds at all points of the cross-section, and from the surface-stress equation

$$l(\hat{x}) + m(\hat{y}) = 0,$$

that is,

$$\frac{dw}{d\rho} + (mx - ly)\tau = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

at the boundary, where du is an element of the outwards normal, and (l, m) are its direction-cosines.

The above conditions allow us to determine w uniquely. They are associated with the condition that the parallel to the generators through the origin remains fixed. If, however, we take any other parallel to the generators through the point (a, b) to remain fixed, then

$$u = -\tau(y-b)z, \quad v = \tau(x-a)z,$$

$$\frac{\widehat{yz}}{\mu} = \frac{dw}{dy} + \tau(x-a), \quad \frac{\widehat{xz}}{\mu} = \frac{dw}{dx} - \tau(y-b),$$

and the equation at the boundary becomes

$$\frac{dw}{du} + (mx - ly)\tau - \tau(am - lb) = 0.$$

Now, if instead of w we write

$$w = w' + \tau (ay - bx),$$

then

$$\frac{\widehat{g}_z}{\mu} = \frac{dr'}{dy} + \tau x, \quad \frac{\widehat{g}_z}{\mu} = \frac{dr'}{dx} - \tau y,$$

and the equations to determine w' are the same which we had before for w . It follows that the *stresses* in the cylinder are unaltered, whatever be the parallel to the generators about which it is twisted, the effect of the change being merely to introduce a term $\tau (ay - bx)$ into w , which corresponds to a rigid rotation about an axis joining (a, b) to the origin.

It follows from this that in dealing with stresses due to torsion we may take our origin wherever it is most convenient.

§ 4. *Analytical Work for Sections Bounded by One Elliptic and Two Hyperbolic Arcs.*

Consider now the transformation

$$x = c \cosh \xi \sin \eta,$$

$$y = c \sinh \xi \cos \eta.$$

If we allow η to vary between β and β' , and ξ between $+\alpha$ and $-\alpha$, the point (x, y) will move within the space contained between the ellipse

$$\frac{x^2}{c^2 \cosh^2 \alpha} + \frac{y^2}{c^2 \sinh^2 \alpha} = 1,$$

and the two hyperbolas

$$\frac{x^2}{c^2 \sin^2 \beta} - \frac{y^2}{c^2 \cos^2 \beta} = 1, \quad \frac{x^2}{c^2 \sin^2 \beta'} - \frac{y^2}{c^2 \cos^2 \beta'} = 1.$$

Using then the coordinates (ξ, η) instead of (x, y) we find that our equations for w become

$$\frac{d^2 w}{d\xi^2} + \frac{d^2 w}{d\eta^2} = 0 \quad \text{for} \quad \left\{ \begin{array}{l} \beta' < \eta < \beta \\ -\alpha < \xi < \alpha \end{array} \right\} \quad \dots \quad (3').$$

Also

$$\left. \begin{array}{l} \frac{dw}{d\xi} + \frac{1}{2}\tau c^2 \sin 2\eta = 0, \quad \text{when } \xi = \pm \alpha, \quad \beta' < \eta < \beta \\ \frac{dw}{d\eta} - \frac{1}{2}\tau c^2 \sinh 2\xi = 0, \quad \text{when } \eta = \beta \text{ or } \beta', \quad -\alpha < \xi < \alpha \end{array} \right\} \quad \dots \quad (4').$$

Write now

$$w = w_1 - \frac{1}{4}\tau c^2 \frac{\sinh 2\xi \sin 2\eta}{\cosh 2\alpha}.$$

Then

$$dw_1/d\xi = 0, \quad \xi = \pm \alpha, \quad \beta' < \eta < \beta \quad \dots \quad (5).$$

$$\left. \begin{array}{l} \frac{dw_1}{d\eta} - \frac{1}{2}\tau c^2 \sinh 2\xi \left(1 + \frac{\cos 2\beta}{\cosh 2\alpha} \right) = 0, \quad \eta = \beta, \quad -\alpha < \xi < \alpha \\ \frac{dw_1}{d\eta} - \frac{1}{2}\tau c^2 \sinh 2\xi \left(1 + \frac{\cos 2\beta'}{\cosh 2\alpha} \right) = 0, \quad \eta = \beta', \quad -\alpha < \xi < \alpha \end{array} \right\} \quad \dots \quad (6).$$

Let us assume

$$w_1 = \sum_{n=0}^{\infty} \left(A_n \sinh \frac{2n+1\pi}{2\alpha} (\eta - \epsilon) + B_n \cosh \frac{2n+1\pi(\eta - \epsilon)}{2\alpha} \right) \sin \frac{2n+1\pi\xi}{2\alpha},$$

where $\epsilon = \frac{1}{2}(\beta + \beta')$.

Then conditions (5) and (3') are identically satisfied. Let us now determine the coefficients A and B so that (6) shall also be satisfied.

We have to expand $\sinh 2\xi$ between the limits $\pm \alpha$ in a series of sines as follows :

$$\sinh 2\xi = a_0 \sin \frac{\pi \xi}{2\alpha} + a_1 \sin \frac{3\pi \xi}{2\alpha} + \dots + a_n \sin \frac{(2n+1)\pi \xi}{2\alpha} + \dots$$

The coefficients $a_0, a_1, \dots, a_n, \dots$ are found in the usual way

$$a_n = \frac{1}{\alpha} \int_{-\alpha}^{\alpha} \sinh 2\xi \sin \frac{(2n+1)\pi \xi}{2\alpha} d\xi = (-1)^n \frac{16\alpha \cosh 2\alpha}{\pi^2 (2n+1)^2 + 16\alpha^2},$$

also we have, substituting in (6), equating coefficients of $\sin \frac{(2n+1)\pi \xi}{2\alpha}$, and writing $\beta - \beta' = 2\gamma$,

$$A_n \cosh \frac{(2n+1)\pi \gamma}{2\alpha} + B_n \sinh \frac{(2n+1)\pi \gamma}{2\alpha} = \frac{\tau c^2 \alpha}{(2n+1)\pi} a_n \left(1 + \frac{\cos 2\beta}{\cosh 2\alpha} \right),$$

$$A_n \cosh \frac{(2n+1)\pi \gamma}{2\alpha} - B_n \sinh \frac{(2n+1)\pi \gamma}{2\alpha} = \frac{\tau c^2 \alpha}{(2n+1)\pi} a_n \left(1 + \frac{\cos 2\beta'}{\cosh 2\alpha} \right),$$

whence, solving for A_n and B_n , we find

$$A_n = \frac{16\tau c^2 \alpha^2}{(2n+1)\pi} (-1)^n \frac{\operatorname{sech} \frac{(2n+1)\pi \gamma}{2\alpha}}{\pi^2 (2n+1)^2 + 16\alpha^2} (\cosh 2\alpha + \cos 2\epsilon \cos 2\gamma) \dots \quad (7).$$

$$B_n = - \frac{16\tau c^2 \alpha^2}{(2n+1)\pi} (-1)^n \frac{\operatorname{cosech} \frac{(2n+1)\pi \gamma}{2\alpha}}{\pi^2 (2n+1)^2 + 16\alpha^2} \sin 2\epsilon \sin 2\gamma \dots \quad (8).$$

whence

$$\begin{aligned} w = & -\frac{1}{4} \tau c^2 \frac{\sinh 2\xi \sin 2\eta}{\cosh 2\alpha} \\ & + 16\tau c^2 \alpha^2 \{ \cosh 2\alpha + \cos 2\epsilon \cos 2\gamma \} \sum_{n=0}^{\infty} (-1)^n \frac{\sinh \frac{(2n+1)\pi}{2\alpha} (\eta - \epsilon) \sin \frac{(2n+1)\pi \xi}{2\alpha}}{\pi (2n+1) [\pi^2 (2n+1)^2 + 16\alpha^2] \cosh \frac{(2n+1)\pi \gamma}{2\alpha}} \\ & - 16\tau c^2 \alpha^2 \sin 2\gamma \sin 2\epsilon \sum_{n=0}^{\infty} (-1)^n \frac{\cosh \frac{(2n+1)\pi}{2\alpha} (\eta - \epsilon) \sin \frac{(2n+1)\pi \xi}{2\alpha}}{\pi (2n+1) [\pi^2 (2n+1)^2 + 16\alpha^2] \sinh \frac{(2n+1)\pi \gamma}{2\alpha}} \dots \quad (9). \end{aligned}$$

Having obtained w , the shears are easily deduced by simple differentiation

$$\left. \begin{aligned} \frac{\widehat{xz}}{\mu} &= \frac{1}{cJ} \left(\sinh \xi \sin \eta \frac{dw}{d\xi} + \cosh \xi \cos \eta \frac{dw}{d\eta} \right) - \tau c \sinh \xi \cos \eta \\ \frac{\widehat{yz}}{\mu} &= \frac{1}{cJ} \left(\cosh \xi \cos \eta \frac{dw}{d\xi} - \sinh \xi \sin \eta \frac{dw}{d\eta} \right) + \tau c \cosh \xi \sin \eta \end{aligned} \right\} \quad (10),$$

where $J = \cosh^2 \xi \cos^2 \eta + \sinh^2 \xi \sin^2 \eta$.

These again may be put into the slightly different form

$$\left. \begin{aligned} \frac{\widehat{xz}}{\mu} &= \frac{1}{cJ} \left(\sinh \xi \sin \eta \frac{dw_1}{d\xi} + \cosh \xi \cos \eta \frac{dw_1}{d\eta} \right) - \tau c \sinh \xi \cos \eta (1 + \operatorname{sech} 2\alpha) \\ \frac{\widehat{yz}}{\mu} &= \frac{1}{cJ} \left(\cosh \xi \cos \eta \frac{dw_1}{d\xi} - \sinh \xi \sin \eta \frac{dw_1}{d\eta} \right) + \tau c \cosh \xi \sin \eta (1 - \operatorname{sech} 2\alpha). \end{aligned} \right.$$

The next quantity which we require is the moment of the shears

$$\begin{aligned} M &= \int (x\widehat{yz} - y\widehat{xz}) dx dy \\ &= \frac{\mu\tau c^4}{2} \int_{\beta'}^{\beta} d\eta \int_{-a}^a d\xi [(\cosh 2\xi - \cos 2\eta) - \operatorname{sech} 2\alpha (1 - \cosh 2\xi \cos 2\eta)] \times J \\ &\quad + \frac{\mu c^2}{2} \int_{\beta'}^{\beta} d\eta \int_{-a}^a d\xi \left[\frac{dw_1}{d\xi} \sin 2\eta - \frac{dw_1}{d\eta} \sinh 2\xi \right] \\ &= \frac{\mu\tau c^4}{8} \int_{\beta'}^{\beta} d\eta \int_{-a}^a d\xi (\cosh 4\xi - \cos 4\eta - \operatorname{sech} 2\alpha \{ \cosh 2\xi + \cos 2\eta \} \\ &\quad + \operatorname{sech} 2\alpha \{ \cosh 4\xi \cos 2\eta + \cosh 2\xi \cos 4\eta \}) \\ &\quad + \frac{\mu c^2}{2} \int_{\beta'}^{\beta} d\eta \sin 2\eta \left[w_1 \right]_{-a}^a - \frac{\mu c^2}{2} \int_{-a}^a d\xi \sinh 2\xi \left[w_1 \right]_{\beta'}^{\beta} \\ &= \frac{\mu\tau c^4}{8} \left[\gamma \sinh 4\alpha - \alpha \sin 4\gamma \cos 4\epsilon - \operatorname{sech} 2\alpha (2\gamma \sinh 2\alpha + 2\alpha \sin 2\gamma \cos 2\epsilon) \right. \\ &\quad \left. + \frac{\operatorname{sech} 2\alpha}{2} (\sinh 4\alpha \cos 2\epsilon \sin 2\gamma + \sinh 2\alpha \cos 4\epsilon \sin 4\gamma) \right] \\ &\quad + \sum_{n=0}^{\infty} \frac{16\mu\tau c^4 \alpha^2 (\cosh 2\alpha + \cos 2\epsilon \cos 2\gamma)}{\pi (2n+1) [\pi^2 (2n+1)^2 + 16\alpha^2] \cosh \frac{2n+1\pi\gamma}{2\alpha}} \int_{\beta'}^{\beta} \sinh \frac{2n+1\pi}{2\alpha} (\eta - \epsilon) \sin 2\eta d\eta \\ &\quad - \sum_{n=0}^{\infty} \frac{16\mu\tau c^4 \alpha^2 \sin 2\gamma \sin 2\epsilon}{\pi (2n+1) [\pi^2 (2n+1)^2 + 16\alpha^2] \sinh \frac{2n+1\pi\gamma}{2\alpha}} \int_{\beta'}^{\beta} \cosh \frac{2n+1\pi}{2\alpha} (\eta - \epsilon) \sin 2\eta d\eta \\ &\quad - \sum_{n=0}^{\infty} \frac{16\mu\tau c^4 \alpha^2 (\cosh 2\alpha + \cos 2\epsilon \cos 2\gamma) (-1)^n \tanh \frac{2n+1\pi\gamma}{2\alpha}}{\pi (2n+1) [\pi^2 (2n+1)^2 + 16\alpha^2]} \int_{-a}^a \sin \frac{2n+1\pi\xi}{2\alpha} \sinh 2\xi d\xi. \end{aligned}$$

$$\begin{aligned}
&= \frac{\mu\tau c^4}{8} \left[\gamma \sinh 4\alpha - \alpha \sin 4\gamma \cos 4\epsilon - \operatorname{sech} 2\alpha \{ 2\gamma \sinh 2\alpha + 2\alpha \sin 2\gamma \cos 2\epsilon \} \right. \\
&\quad \left. + \frac{\operatorname{sech} 2\alpha}{2} \{ \sinh 4\alpha \sin 2\gamma \cos 2\epsilon + \sinh 2\alpha \sin 4\gamma \cos 4\epsilon \} \right] \\
&\quad - 256\mu\tau c^4 \alpha' (\cosh 2\alpha + \cos 2\epsilon \cos 2\gamma)^2 \sum_{n=0}^{\infty} \frac{\tanh \frac{2n+1\pi\gamma}{2\alpha}}{\pi(2n+1)[\pi^2(2n+1)^2 + 16\alpha^2]^2} \\
&\quad - 256\mu\tau c^4 \alpha' (\sin 2\epsilon \sin 2\gamma)^2 \sum_{n=0}^{\infty} \frac{\coth \left(\frac{2n+1\pi\gamma}{2\alpha} \right)}{\pi(2n+1)[\pi^2(2n+1)^2 + 16\alpha^2]^2} \\
&\quad + 64\mu\tau c^4 \alpha^3 \sin 2\gamma (\cosh 2\alpha \cos 2\epsilon + \cos 2\gamma \cos 4\epsilon) \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2 \pi^2 + 16\alpha^2]^2}.
\end{aligned}$$

But the series $\sum_0^{\infty} \frac{1}{[(2n+1)^2 \pi^2 + 16\alpha^2]^2}$ can be summed in finite terms,* and it is found to be

$$-\frac{1}{512\alpha^3} (2\alpha \operatorname{sech}^2 2\alpha - \tanh 2\alpha).$$

Substituting this value in the expression for the torsion moment we find

$$\begin{aligned}
M &= \frac{\mu\tau c^4}{8} \left[(\gamma \sinh 4\alpha - \alpha \sin 4\gamma \cos 4\epsilon) (1 - \operatorname{sech}^2 2\alpha) \right. \\
&\quad - \alpha \sin 4\gamma \cos 4\epsilon \operatorname{sech}^2 2\alpha - 2\alpha \operatorname{sech} 2\alpha \sin 2\gamma \cos 2\epsilon \\
&\quad + \operatorname{sech} 2\alpha [\sinh 2\alpha \sin 2\gamma] (\cosh 2\alpha \cos 2\epsilon + \cos 2\gamma \cos 4\epsilon) \\
&\quad \left. - \sin 2\gamma (2\alpha \operatorname{sech}^2 2\alpha - \tanh 2\alpha) (\cosh 2\alpha \cos 2\epsilon + \cos 2\gamma \cos 4\epsilon) \right] \\
&\quad - \text{the two series terms.}
\end{aligned}$$

Whence, after some obvious reductions

$$\begin{aligned}
\frac{M}{\mu\tau c^4} &= \frac{\tanh^2 2\alpha}{8} (\gamma \sinh 4\alpha - \alpha \sin 4\gamma \cos 4\epsilon) \\
&\quad - \frac{1}{4} \sin 2\gamma (\cosh 2\alpha \cos 2\epsilon + \cos 2\gamma \cos 4\epsilon) (2\alpha \operatorname{sech}^2 2\alpha - \tanh 2\alpha) \\
&\quad - 256\alpha^4 (\cosh 2\alpha + \cos 2\epsilon \cos 2\gamma)^2 \sum_{n=0}^{\infty} \frac{\tanh \frac{2n+1\pi\gamma}{2\alpha}}{\pi(2n+1)[16\alpha^2 + 2n+1\pi^2]^2} \\
&\quad - 256\alpha^4 (\sin 2\gamma \sin 2\epsilon)^2 \sum_{n=0}^{\infty} \frac{\coth \frac{2n+1\pi\gamma}{2\alpha}}{\pi(2n+1)[16\alpha^2 + 2n+1\pi^2]^2} \dots \dots \dots (11).
\end{aligned}$$

* See CHRYSTAL'S 'Algebra,' vol. 2 (Differentiating the result marked (8) on p. 338).

§ 5. *Alternative Solution for the same Sections.*

There exists also an alternative solution ; it is generally of a less convenient form than the one last given. It may, however, be useful in certain cases.

Return now to the boundary conditions (4') and write

$$w = w_1 + \frac{1}{4}rc^2 \frac{\sinh 2\xi \sin 2(\eta - \epsilon)}{\cos 2\gamma}$$

we then obtain

$$\frac{dw_1}{d\eta} = 0 \quad \text{when} \quad \eta = \beta \quad \text{or} \quad \eta = \beta', \quad -\alpha < \xi < +\alpha$$

and

$$\frac{dw_1}{d\xi} + \frac{1}{2}rc^2 \left\{ \sin 2\eta + \frac{\cosh 2\alpha}{\cos 2\gamma} \sin 2(\eta - \epsilon) \right\} = 0,$$

when

$$\xi = \pm \alpha, \quad \beta' < \eta < \beta.$$

The latter condition may be written

$$\frac{dw_1}{d\xi} + \frac{1}{2}rc^2 \left[\sin 2(\eta - \epsilon) \frac{(\cosh 2\alpha + \cos 2\gamma \cos 2\epsilon)}{\cos 2\gamma} + \cos 2(\eta - \epsilon) \cdot \sin 2\epsilon \right] = 0.$$

Now let us write

$$w_1 = \varpi_1 + \varpi_2$$

where

$$\frac{d^2\varpi_1}{d\xi^2} + \frac{d^2\varpi_1}{d\eta^2} = 0, \quad \frac{d^2\varpi_2}{d\xi^2} + \frac{d^2\varpi_2}{d\eta^2} = 0,$$

and

$$d\varpi_1/d\eta = 0, \quad \eta - \epsilon = \pm \gamma \quad d\varpi_2/d\eta = 0, \quad \eta - \epsilon = \pm \gamma.$$

But

$$\frac{d\varpi_1}{d\xi} + \frac{1}{2}rc^2 \sin 2(\eta - \epsilon) \left(\frac{\cosh 2\alpha + \cos 2\gamma \cos 2\epsilon}{\cos 2\gamma} \right) = 0 \quad \dots \dots (12)$$

$$\frac{d\varpi_2}{d\xi} + \frac{1}{2}rc^2 \cos 2(\eta - \epsilon) \sin 2\epsilon = 0 \quad \dots \dots (13)$$

when

$$\xi = \pm \alpha \quad \text{and} \quad -\gamma < \eta - \epsilon < +\gamma.$$

Assume

$$\varpi_1 = \sum_{n=0}^{\infty} A_n \sinh \frac{2n+1\pi\xi}{2\gamma} \sin \frac{2n+1\pi(\eta-\epsilon)}{2\gamma}$$

$$\varpi_2 = B_0\xi + \sum_{n=1}^{\infty} B_n \sinh \frac{n\pi\xi}{\gamma} \cos \frac{n\pi(\eta-\epsilon)}{\gamma},$$

we have now to express between limits $\pm \gamma$

$$\cos 2\theta = b_0 + b_1 \cos \frac{\pi\theta}{\gamma} + b_2 \cos \frac{2\pi\theta}{\gamma} + \dots + b_n \cos \frac{n\pi\theta}{\gamma} + \dots$$

$$\sin 2\theta = a_1 \sin \frac{\pi\theta}{2\gamma} + a_2 \sin \frac{3\pi\theta}{2\gamma} + \dots + a_n \sin \frac{(2n+1)\pi\theta}{2\gamma} + \dots$$

We find

$$b_n = (-1)^{n+1} \frac{4\gamma \sin 2\gamma}{n^2\pi^2 - 4\gamma^2}, \quad a_n = (-1)^n \frac{16\gamma \cos 2\gamma}{(2n+1)^2\pi^2 - 16\gamma^2}$$

$$b_0 = \frac{1}{2\gamma} \sin 2\gamma$$

Substituting in (12) and (13) and equating coefficients we obtain

$$A_n = - \frac{16\tau c^2 \gamma^2 (\cosh 2\alpha + \cos 2\gamma \cos 2\epsilon) (-1)^n}{(2n+1)\pi [(2n+1)^2\pi^2 - 16\gamma^2]} \operatorname{sech} \frac{(2n+1)\pi\alpha}{2\gamma},$$

$$B_n = \frac{2\tau c^2 \gamma^2 \sin 2\epsilon \sin 2\gamma (-1)^n}{n\pi (n^2\pi^2 - 4\gamma^2)} \operatorname{sech} \frac{n\pi\alpha}{\gamma},$$

$$B_0 = - \frac{1}{4\gamma} \tau c^2 \sin 2\gamma \sin 2\epsilon,$$

whence

$$w = \frac{1}{4}\tau c^2 \frac{\sinh 2\xi \sin 2(\eta - \epsilon)}{\cos 2\gamma}$$

$$+ 16\tau c^2 \gamma^2 \sin 2\epsilon \sin 2\gamma \left[- \frac{\xi}{64\gamma^2} + \sum_{n=1}^{\infty} (-1)^n \frac{\sinh \frac{n\pi\xi}{\gamma} \cos \frac{n\pi(\eta - \epsilon)}{\gamma}}{2n\pi (4n^2\pi^2 - 16\gamma^2) \cosh \frac{n\pi\alpha}{\gamma}} \right]$$

$$- 16\tau c^2 \gamma^2 (\cosh 2\alpha + \cos 2\gamma \cos 2\epsilon)$$

$$\times \left[\sum_{n=0}^{\infty} (-1)^n \frac{\sinh \frac{(2n+1)\pi\xi}{2\gamma} \sin \frac{(2n+1)\pi(\eta - \epsilon)}{2\gamma}}{(2n+1)\pi [(2n+1)^2\pi^2 - 16\gamma^2] \cosh \frac{(2n+1)\pi\alpha}{2\gamma}} \right] \dots \dots \dots (14).$$

It may be noted here that γ may vary between 0 and $\pi/2$. It follows that γ may have the value $\pi/2$, and in that case the denominator of the first term under the first Σ becomes zero. The same happens to the denominator of the first term of the second Σ when γ has the value $\pi/4$. Further, in this latter case the first term in w also becomes infinite, so that the expression (14) is apparently no longer applicable.

It is easy to see, however, that the terms, which are apparently infinite in (14), exactly cancel each other. If we write $\gamma = \pi/4 - \zeta$, where ζ is small, simplify and proceed to the limit, we find that when $\gamma = \pi/4$ the two infinite terms reduce to:

$$\frac{1}{4}\tau c^2 \sinh 2\xi \sin 2(\eta - \epsilon) \left[\frac{\cos 2\epsilon}{\cosh 2\alpha} - \frac{4}{\pi} - \frac{4\alpha}{\pi} \tanh 2\alpha \right]$$

$$+ \frac{\tau c^2}{\pi} [\xi \cosh 2\xi \sin 2(\eta - \epsilon) + (\eta - \epsilon) \cos 2(\eta - \epsilon) \sinh 2\xi] \dots \dots (15),$$

which is finite.

In like manner when $\gamma = \pi/2$ the limit of w is easily evaluated.

For all *other* values of γ , ϵ and α the series in (14) are absolutely convergent as they stand, for all points (ξ, η) *within* or *on* the boundary of the section. The same holds of all the series in the last paragraph for *all* values of α , γ , ϵ .

The expression for w being given, the shears and torsion moment are obtained as before

$$M = \frac{\mu\tau c^4}{8} \int_{\beta'}^{\beta} d\eta \int_{-a}^a d\xi (\cosh 4\xi - \cos 4\eta) + \frac{\mu c^2}{2} \int_{\beta'}^{\beta} [w]_{-a}^a \sin 2\eta d\eta - \frac{\mu c^2}{2} \int_{-a}^a [w]_{\beta'}^{\beta} \sinh 2\xi d\xi.$$

The integrations are all easily effected, and we find

$$\begin{aligned} M = & \frac{\mu\tau c^4}{8} (\gamma \sinh 4\alpha - \alpha \sin 4\gamma \cos 4\epsilon) \\ & + \frac{\mu\tau c^4}{4} \frac{(\alpha \sin 2\gamma + \gamma \sinh 2\alpha \cos 2\epsilon)}{\cos 2\gamma} - \frac{1}{16} \frac{\mu\tau c^4 (\sinh 4\alpha \sin 2\gamma + \sinh 2\alpha \sin 4\gamma \cos 2\epsilon)}{\cos 2\gamma} \\ & + 64\mu\tau c^4 \gamma^3 (\cosh 2\alpha + \cos 2\gamma \cos 2\epsilon) \sinh 2\alpha \sum_{n=0}^{\infty} \frac{1}{[(2n+1)^2 \pi^2 - 16\gamma^2]^2} \\ & - 256\mu\tau c^4 \gamma^4 (\cosh 2\alpha + \cos 2\gamma \cos 2\epsilon)^2 \sum_{n=0}^{\infty} \frac{\tanh \frac{(2n+1)\pi\alpha}{2\gamma}}{(2n+1)\pi [\pi^2 (2n+1)^2 - 16\gamma^2]^2} \\ & - 256\mu\tau c^4 \gamma^4 (\sin 2\epsilon \sin 2\gamma)^2 \left\{ \sum_{n=1}^{\infty} \frac{\tanh \frac{n\pi\alpha}{\gamma}}{2n\pi (4n^2 \pi^2 - 16\gamma^2)^2} + \frac{\alpha}{1024\gamma^5} \right\}. \end{aligned}$$

Remembering that $\sum_{n=0}^{\infty} \frac{1}{\{(2n+1)^2 \pi^2 - 16\gamma^2\}^2} = \frac{2\gamma \sec^2 2\gamma - \tan 2\gamma}{512\gamma^3}$, reducing, and re-grouping the terms, we find finally

$$\begin{aligned} \frac{M}{\mu\tau c^4} = & \frac{1}{8} (\alpha \sin 4\gamma - \gamma \sinh 4\alpha) \tan^2 2\gamma \\ & + \frac{1}{4} (\cosh 2\alpha + \cos 2\gamma \cos 2\epsilon) (2\gamma \sec^2 2\gamma - \tan 2\gamma) \sinh 2\alpha \\ & + \frac{\alpha}{8\gamma} \sin 4\gamma \sin^2 2\epsilon (2\gamma - \tan 2\gamma) \\ & - 256\gamma^4 (\cosh 2\alpha + \cos 2\gamma \cos 2\epsilon)^2 \sum_{n=0}^{\infty} \frac{\tanh \frac{(2n+1)\pi\alpha}{2\gamma}}{2n+1 [\pi^2 (2n+1)^2 - 16\gamma^2]^2} \\ & - 256\gamma^4 (\sin 2\epsilon \sin 2\gamma)^2 \sum_{n=1}^{\infty} \frac{\tanh \frac{n\pi\alpha}{\gamma}}{2n\pi (4n^2 \pi^2 - 16\gamma^2)^2} \dots \dots \dots (16). \end{aligned}$$

We may test the correctness of the expressions (11) and (16) by remembering that

when we make the distance c between the foci very great, and γ and α very small, the section reduces to a rectangle, of which the half sides a and b are given by

$$a = c\alpha \cos \epsilon, \quad b = c\gamma \cos \epsilon.$$

The first and last terms in (16) are ultimately of negligible order, when multiplied by c^4 .

The second and third reduce to

$$\begin{aligned} \frac{8}{3} \gamma^3 \alpha (1 + \cos 2\epsilon) - \frac{8}{3} \gamma^3 \alpha (1 - \cos 4\epsilon) &= \frac{8}{3} \gamma^3 \alpha (3 + 4 \cos 2\epsilon + \cos 4\epsilon) \\ &= \frac{16}{3} \gamma^3 \alpha \cos^4 \epsilon. \end{aligned}$$

The fourth term gives

$$- 1024 (\gamma \cos \epsilon)^4 \sum_{n=0}^{\infty} \frac{\tanh \frac{2n+1\pi a}{2b}}{(2n+1)^5 \pi^5}.$$

Hence

$$\frac{M}{\mu \tau b^4} = \frac{16}{3} \frac{a}{b} - \left(\frac{4}{\pi} \right)^5 \sum_{n=0}^{\infty} \frac{\tanh \frac{2n+1\pi a}{2b}}{(2n+1)^5} \dots$$

which is one of SAINT-VENANT'S expressions for the torsion moment of a rectangle of sides $2a$, $2b$.

If we treat in a similar manner expression (11), neglecting terms of order greater than four in α , γ , we get the other expression for the torsion moment of the rectangle.

§ 6. *Recapitulation of Results for the Symmetrical Case.*

By far the most important case we have to deal with is that in which the sections are symmetrical.

We have then $\beta' = -\beta$, and therefore $\epsilon = 0$, $\gamma = \beta$.

Both solutions then simplify a good deal, and we have the equivalent expressions

$$\begin{aligned} w &= -\frac{1}{4} \tau c^2 \sinh 2\xi \sin 2\eta \operatorname{sech} 2\alpha \\ &+ 16\tau c^2 \alpha^2 (\cosh 2\alpha + \cos 2\beta) \sum_{n=0}^{\infty} \frac{(-1)^n \sinh \frac{2n+1\pi\eta}{2\alpha} \sin \frac{2n+1\pi\xi}{2\alpha}}{\pi(2n+1) [(2n+1)^2 \pi^2 + 16\alpha^2] \cosh \frac{2n+1\pi\beta}{2\alpha}} \\ &= \frac{1}{4} \tau c^2 \sinh 2\xi \sin 2\eta \sec 2\beta \\ &- 16\tau c^2 \beta^2 (\cosh 2\alpha + \cos 2\beta) \sum_{n=0}^{\infty} \frac{(-1)^n \sinh \frac{2n+1\pi\xi}{2\beta} \sin \frac{2n+1\pi\eta}{2\beta}}{\pi(2n+1) [(2n+1)^2 \pi^2 - 16\beta^2] \cosh \frac{2n+1\pi\alpha}{2\beta}}. \quad (17). \end{aligned}$$

$$\begin{aligned}
\frac{\widehat{wz}}{\mu} &= -\tau c \sinh \xi \cos \eta (1 + \operatorname{sech} 2\alpha) + 32\tau c \alpha^2 \frac{(\cosh 2\alpha + \cos 2\beta)}{(\cosh 2\xi + \cos 2\eta)} \\
&\quad \times \sum_{n=0}^{\infty} \frac{(-1)^n \left(\sinh \xi \sin \eta \frac{d}{d\xi} + \cosh \xi \cos \eta \frac{d}{d\eta} \right) \sinh \frac{2n+1\pi\eta}{2\alpha} \sin \frac{2n+1\pi\xi}{2\alpha}}{\pi (2n+1) [(2n+1)^2 \pi^2 + 16\alpha^2] \cosh \frac{2n+1\pi\beta}{2\alpha}} \\
&= -\tau c \sinh \xi \cos \eta (1 - \sec 2\beta) - 32\tau c \beta^2 \frac{(\cosh 2\alpha + \cos 2\beta)}{(\cosh 2\xi + \cos 2\eta)} \\
&\quad \times \sum_{n=0}^{\infty} \frac{(-1)^n \left(\sinh \xi \sin \eta \frac{d}{d\xi} + \cosh \xi \cos \eta \frac{d}{d\eta} \right) \sinh \frac{2n+1\pi\xi}{2\beta} \sin \frac{2n+1\pi\eta}{2\beta}}{\pi (2n+1) [(2n+1)^2 \pi^2 - 16\beta^2] \cosh \frac{2n+1\pi\alpha}{2\beta}}. \quad (18).
\end{aligned}$$

$$\begin{aligned}
\frac{\widehat{yz}}{\mu} &= \tau c \cosh \xi \sin \eta (1 - \operatorname{sech} 2\alpha) + 32\tau c \alpha^2 \frac{(\cosh 2\alpha + \cos 2\beta)}{(\cosh 2\xi + \cos 2\eta)} \\
&\quad \times \sum_{n=0}^{\infty} \frac{(-1)^n \left(\cosh \xi \cos \eta \frac{d}{d\xi} - \sinh \xi \sin \eta \frac{d}{d\eta} \right) \sinh \frac{2n+1\pi\eta}{2\alpha} \sin \frac{2n+1\pi\xi}{2\alpha}}{\pi (2n+1) [\pi^2 (2n+1)^2 + 16\alpha^2] \cosh \frac{2n+1\pi\beta}{2\alpha}} \\
&= \tau c \cosh \xi \sin \eta (1 + \sec 2\beta) - 32\tau c \beta^2 \frac{(\cosh 2\alpha + \cos 2\beta)}{(\cosh 2\xi + \cos 2\eta)} \\
&\quad \times \sum_{n=0}^{\infty} \frac{(-1)^n \left(\cosh \xi \cos \eta \frac{d}{d\xi} - \sinh \xi \sin \eta \frac{d}{d\eta} \right) \sinh \frac{2n+1\pi\xi}{2\beta} \sin \frac{2n+1\pi\eta}{2\beta}}{\pi (2n+1) [\pi^2 (2n+1)^2 - 16\beta^2] \cosh \frac{2n+1\pi\alpha}{2\beta}}. \quad (19).
\end{aligned}$$

$$\begin{aligned}
\frac{M}{\mu \tau c^4} &= \frac{\tanh^2 2\alpha}{8} (\beta \sinh 4\alpha - \alpha \sin 4\beta) \\
&\quad - \frac{1}{4} \sin 2\beta (\cosh 2\alpha + \cos 2\beta) (2\alpha \operatorname{sech}^2 2\alpha - \tanh 2\alpha) \\
&\quad - 256\alpha^4 (\cosh 2\alpha + \cos 2\beta)^2 \sum_{n=0}^{\infty} \frac{\tanh \frac{2n+1\pi\beta}{2\alpha}}{\pi (2n+1) [16\alpha^2 + (2n+1)^2 \pi^2]^2} \\
&= \frac{\tan^2 2\beta}{8} (\alpha \sin 4\beta - \beta \sinh 4\alpha) \\
&\quad + \frac{1}{4} \sinh 2\alpha (\cosh 2\alpha + \cos 2\beta) (2\beta \sec^2 2\beta - \tan 2\beta) \\
&\quad - 256\beta^4 (\cosh 2\alpha + \cos 2\beta)^2 \sum_{n=0}^{\infty} \frac{\tanh \frac{2n+1\pi\alpha}{2\beta}}{\pi (2n+1) [2n+1)^2 \pi^2 - 16\beta^2]^2}. \quad (20).
\end{aligned}$$

§ 7. *Importance of the Maximum Stress. Application to Rupture.*

I now pass on to the numerical determination of the torsion moment and stresses, and in particular of the maximum stress.

SAINT-VENANT has shown, in his memoir on torsion,* that if we assume an ellipsoidal distribution of *limiting* stretch (i.e., stretch such that, when it is exceeded, the elasticity of the material is impaired), then, in the case of a shaft under torsion, we have at any point

$$s/\bar{s} = \sqrt{(\sigma_{yz}^2 + \sigma_{xz}^2)/\sigma_0^2},$$

where σ_{yz} , σ_{xz} are the shearing strains in the planes yz , xz respectively, \bar{s} is the value of the *limiting shearing strain* of the material, and s/\bar{s} is the maximum value of the ratio of the stretch in any direction to the *limiting* stretch in that direction.

The condition that there should be no failure of elasticity is therefore that $s/\bar{s} < 1$. Therefore

$$\sigma_{yz}^2 + \sigma_{xz}^2 < \sigma_0^2,$$

and, since $\sigma_{yz} = \widehat{yz}/\mu$, $\sigma_{xz} = \widehat{xz}/\mu$,

$$\widehat{xz}^2 + \widehat{yz}^2 < \mu^2 \sigma_0^2.$$

The points where this condition will first be broken are called by SAINT-VENANT the *fail-points* ("points dangereux"). They are clearly the points where $\widehat{xz}^2 + \widehat{yz}^2$ is a maximum, i.e., where the resultant stress across an element of the section is a maximum. Hence the importance of determining the points of maximum stress. Strictly speaking, the latter give us no certain information as to where, or how, rupture will actually take place: all that they tell us is where linear elasticity begins to fail. But they will, in general, give us a useful clue to the regions where breaking may be expected to occur, and, in the absence of any definite theory of plastic deformation and rupture, we must be content to be guided by the results of elastic theory.

I have worked out numerically the values of the stresses at the points $\xi = \pm \alpha$, $\eta = 0$ and $\xi = 0$, $\eta = \pm \beta$. These give the four points in which the axes meet the boundary of the cross-section. I have denoted them by A and B respectively. The boundary is convex at A and concave at B. From considerations of symmetry it follows that A and B must be points of *maximum* or *minimum* stress, and the stress being zero both at the corners and at the centre, it will often happen that they are points of *maximum* stress. When this is the case those of the points A and B, where the stress is numerically greater, will give us the *fail-points*. But there is an obvious exception, when there are two points of maximum stress on either side of the mid-point, and this is a case which, we shall see, does occur in these sections.

* 'Mémoires des Savants Étrangers,' 1855, vol. xiv., pp. 278-288. See also TODHUNTER and PEARSON, 'Hist. Elast.,' vol. ii., part i., pp. 7-10.

§ 8. *Methods of Calculation.*

The symmetrical sections selected for numerical treatment are those for which $\beta = \pi/6, \pi/4, \pi/3, \pi/2$ and $\alpha = \pi/6, \pi/3, \pi/2$, and $2\pi/3$, sixteen in all. These sections are shown in figs. 2 to 5. β of course is the complement of the half angle between the asymptotes, and all sections having the same β have been collected in one figure.

The numerical calculations were generally based upon the formulæ of § 4, as they did not require modification for the value $\pi/4$ of β . In many cases, however, the alternative series were used also, in order to test the results obtained.

The calculation of the terms of the series in the expression for the torsion moment was carried on until $\frac{2n+1\pi\alpha}{2\beta}$ was so great that $\tanh \frac{2n+1\pi\alpha}{2\beta}$ could be taken sensibly equal to unity. The remainder of the series, namely,

$$\sum_n \frac{1}{\pi(2n+1) [\pi^2(2n+1)^2 + 16\alpha^2]},$$

was then obtained by expanding the denominator by the binomial theorem, thus

$$\sum_n \frac{1}{\pi^2(2n+1)^2} - 2(16\alpha^2) \sum_n \frac{1}{\pi^4(2n+1)^4} + 3(16\alpha^2)^2 \sum_n \frac{1}{\pi^6(2n+1)^6} - \dots$$

The successive terms were easily calculated from the values of $\sum_0 \frac{1}{n^{2s+1}}$ given in CHRYSTAL'S 'Algebra,' vol. 2, chapter XXX, § 15.

The stresses at A and B were calculated from formulæ (18) and (19). If S_A, S_B denote these stresses, we find easily

$$\begin{aligned} \frac{S_A}{\mu} &= -\tau c \tanh 2\alpha \cosh \alpha + 8\tau c \alpha \left(\frac{\cosh 2\alpha + \cos 2\beta}{\cosh \alpha} \right) \sum_{n=0}^{\infty} \frac{\operatorname{sech} \frac{2n+1\pi\beta}{2\alpha}}{\pi^2(2n+1)^2 + 16\alpha^2} \\ &= \tau c \sinh \alpha (\sec 2\beta - 1) - 8\tau c \beta \left(\frac{\cosh 2\alpha + \cos 2\beta}{\cosh \alpha} \right) \sum_{n=0}^{\infty} \frac{(-1)^n \tanh \frac{2n+1\pi\alpha}{2\beta}}{\pi^2(2n+1)^2 - 16\beta^2}. \quad (21). \end{aligned}$$

$$\begin{aligned} \frac{S_B}{\mu} &= \tau c \sin \beta (1 - \operatorname{sech} 2\alpha) + 8\tau c \alpha \left(\frac{\cosh 2\alpha + \cos 2\beta}{\cos \beta} \right) \sum_{n=0}^{\infty} \frac{(-1)^n \tanh \frac{2n+1\pi\beta}{2\alpha}}{\pi^2(2n+1)^2 + 16\alpha^2} \\ &= \tau c \tan 2\beta \cos \beta - 8\tau c \beta \left(\frac{\cosh 2\alpha + \cos 2\beta}{\cos \beta} \right) \sum_{n=0}^{\infty} \frac{\operatorname{sech} \frac{2n+1\pi\alpha}{2\beta}}{(2n+1)^2 \pi^2 - 16\beta^2} \quad (22). \end{aligned}$$

The first expressions for S_A, S_B were used in each case as the main basis of the calculation, but the results were partly verified by means of the second expressions.

With regard to the accuracy obtained, I may say that, where I was able to verify, I found the values of the stresses correct to five, and sometimes to six, significant figures. In the values of the torsion moment the first five figures generally agreed, so that, on the whole, the results may be considered correct to the number of figures given.

The first series for S_B and the second series for S_A are very slowly convergent indeed. The method adopted in dealing with them was the following:

The series

$$\sum_{n=0}^{\infty} \frac{(-1)^n \tanh \frac{2n+1\pi\beta}{2\alpha}}{\pi^2(2n+1)^2 + 16\alpha^2}$$

was broken up into two series

$$\sum_{n=0}^{\infty} \frac{(-1)^n}{\pi^2(2n+1)^2 + 16\alpha^2} - \sum_{n=0}^{\infty} \frac{(-1)^n \left(1 - \tanh \frac{2n+1\pi\beta}{2\alpha}\right)}{\pi^2(2n+1)^2 + 16\alpha^2}.$$

The latter series converges rapidly, and was easily calculated. The former was calculated to an even number of terms, and the remainder obtained by means of the Euler-Maclaurin sum-formula, thus:

$$\sum_{n=2,4,\dots}^{\infty} \frac{(-1)^n}{\pi^2(2n+1)^2 + 16\alpha^2} = \sum_x \frac{1}{\pi^2(4x+1)^2 + 16\alpha^2} - \sum_x \frac{1}{\pi^2(4x-1)^2 + 16\alpha^2}.$$

Now

$$\Sigma u_x = C + \int u_x dx - \frac{1}{2}u_x + \frac{B_1}{2!} \frac{du_x}{dx} - \frac{B_2}{4!} \frac{d^3u_x}{dx^3} + \dots$$

where $B_1 = \frac{1}{6}$, $B_2 = \frac{1}{30}$, &c.

Let me write

$$\rho^2 = (4x+1)^2 \pi^2 + 16\alpha^2,$$

$$\theta = \tan^{-1} \frac{4\alpha}{(4x+1)\pi}, \quad u_x = \frac{1}{\rho^2}.$$

Then

$$\int u_x dx = -\frac{\theta}{16x\pi} \frac{d^3u_x}{dx^3} = \frac{(-1)^n \sin n + 1\theta}{\rho^{n+1}} \frac{(4\pi)^n n!}{4x},$$

whence

$$\sum_{n=1}^{\infty} u_x = C - \frac{\theta}{16x\pi} - \frac{1}{2\rho^2} - \frac{B_1}{2} \frac{\sin 2\theta}{\rho^2} \cdot \frac{(4\pi)}{4x} + \frac{B_2}{4} \frac{\sin 4\theta}{\rho^4} \frac{(4\pi)^3}{4x} - \dots$$

Put $x = \infty$, $\theta = 0$, $\rho = \infty$,

$$\Sigma u_x = C,$$

therefore,

$$\sum_x u_x = \frac{\theta}{16x\pi} + \frac{1}{2\rho^2} + \frac{B_1}{2} \frac{\sin 2\theta}{\rho^2} \left(\frac{\pi}{x}\right) - \frac{B_2}{4} \cdot \frac{\pi}{x} \cdot \frac{\sin 4\theta}{\rho^4} \cdot 16\pi^2 + \dots$$

In like manner if $r = \frac{1}{\rho'^2}$,

$$\rho'^2 = \pi^2 (4x - 1)^2 + 16\alpha^2,$$

$$\theta' = \tan^{-1} \frac{4\alpha}{(4x - 1)\pi},$$

$$\frac{x}{r} = \frac{\theta'}{16\alpha\pi} + \frac{1}{2\rho'^2} + \frac{B_1 \sin 2\theta'}{2\rho'^2} \left(\frac{\pi}{\alpha}\right) - \frac{B_2}{4} \left(\frac{\pi}{\alpha}\right) \frac{\sin 4\theta'}{\rho'^4} 16\pi^2 + \dots$$

These series converge fairly rapidly if x is at all large, and thus the remainder can be obtained.

Even with the help of all these devices the labour of calculating the moment and stress for the sixteen sections was considerable.

The values of the hyperbolic functions were taken from GUDERMANN'S Tables ('Theorie der Potenzial oder Cyklisch-hyperbolischen Functionen'), and from GLAISHER'S and NEUMAN'S Tables of the Exponential Function ('Cambridge Phil. Trans.,' vol. 13).

§ 9. Values of the Torsional Rigidity.

The first quantity calculated was the torsion moment. The values found are shown in the table below.

TABLE of $M/\mu\tau c^4$.

	$\beta = \pi/6.$	$\pi/4.$	$\pi/3.$	$\pi/2.$
$\alpha = \pi/6$	·1710	·3116	·4055	·4676
$\alpha = \pi/3$	·8764	2·0317	3·2205	4·8117
$\alpha = \pi/2$	3·8798	9·4161	16·442	29·912
$\alpha = 2\pi/3$	22·898	54·824	96·411	194·18

It is interesting to compare this table with the table of values of the torsion moment, as given by DE SAINT-VENANT'S empirical formula, viz.,

$$\text{torsion moment} = \frac{\mu\tau}{40} \frac{A^2}{I},$$

where A = area, I = moment of inertia of section about its centroid.

Calling M' this value of the torsion moment, we have

$$\frac{M'}{\mu\tau c^4} = \frac{1}{5} \frac{(\beta \sinh 2\alpha + \alpha \sin 2\beta)^4}{\beta \sinh 4\alpha - \alpha \sin 4\beta},$$

whence we obtain the following set of values :—

TABLE OF $M'/\mu\tau c^4$.

	$\beta = \pi/6.$	$\pi/4.$	$\pi/3.$	$\pi/2.$
$\alpha = \pi/6$	·1835	·3266	·4152	·4723
$\alpha = \pi/3$	·9914	2·3759	3·8023	6·0121
$\alpha = \pi/2$	4·3368	12·195	23·260	51·500
$\alpha = 2\pi/3$	23·289	71·826	152·96	420·95

If we compare this with the preceding table, we see at once that although the agreement is fairly good for the more compact sections, SAINT-VENANT'S empirical formula utterly breaks down for deeply indented sections. That, indeed, might have been expected, since it takes no account of slits cut into the material. One rather noticeable feature in the comparison is that SAINT-VENANT'S formula always gives too high a value for the torsional rigidity.

§ 10. *Comparison with the Circle. "Relative" Torsional Rigidity.*

In order, however, to compare properly the efficiency or usefulness of these various sections, it was found advisable to refer each of them to some kind of standard, or unit. The most obvious standard, as I thought, was the circular section, this being the one whose torsion obeys the most simple laws. I determined, therefore, to compare every section with the circular section of the same area.

Now if r be the radius of this circular section, its torsion moment $M_0 = \frac{1}{2}\pi\mu\tau r^4$, and the maximum stress $S_0 = \mu\tau r$. To find r , we have the equation :

$$\pi r^2 = \text{area of given section} = c^2(\beta \sinh 2\alpha + \alpha \sinh 2\beta),$$

whence

$$\frac{M_0}{\mu\tau c^4} = \frac{\pi}{2} \left(\frac{\beta \sinh 2\alpha + \alpha \sinh 2\beta}{\pi} \right)^2,$$

$$\frac{S_0}{\mu\tau c} = \left(\frac{\beta \sinh 2\alpha + \alpha \sinh 2\beta}{\pi} \right)^{\frac{1}{2}}.$$

The values of $\left(\frac{\beta \sinh 2\alpha + \alpha \sinh 2\beta}{\pi} \right)$ for the various sections are easily found.

TABLE of $\left(\frac{\beta \sinh 2\alpha + \alpha \sin 2\beta}{\pi}\right)$.

	$\beta = \pi/6$.	$\pi/4$.	$\pi/3$.	$\pi/2$.
$\alpha = \pi/6$	·3526	·4790	·5608	·6247
$\alpha = \pi/3$	·9551	1·3330	1·6216	1·9993
$\alpha = \pi/2$	2·3578	3·3872	4·2826	5·7744
$\alpha = 2\pi/3$	6·0713	8·9076	11·565	16·482

whence we obtain the following table giving us M/M_0 :—

	$\beta = \pi/6$.	$\pi/4$.	$\pi/3$.	$\pi/2$.
$\alpha = \pi/6$	·8756	·8644	·8208	·7628
$\alpha = \pi/3$	·6116	·7279	·7797	·7663
$\alpha = \pi/2$	·4443	·5225	·5707	·5711
$\alpha = 2\pi/3$	·3955	·4399	4590	·4551

When we look at this table, we observe immediately that the torsional rigidity decreases, compared with the torsional rigidity of the circular section, as we increase α , that is to say, as we decrease the thickness of the neck with regard to the other linear dimension. This indeed might have been expected, for it is clear that such a process must weaken the rigidity enormously, inasmuch as it tends to render the two halves of the section independent of each other.

When $\alpha = \pi/6$, $\beta = \pi/6$, the ratio M/M_0 is greatest. In this case the section does not deviate very much from a square. (For very small values of α and β the section is, of course, a rectangle.) This result shows us therefore that, so far as torsional rigidity is concerned, the square is a more efficient form of section than any one of those dealt with in the present paragraph.

That the circle is a more efficient type of section for rigidity is quite evident from the table, since all the values in it are less than unity.

It may be interesting to note what are the values of M/M_0 for the full ellipse. When we use the values given by SAINT-VENANT in his memoir on torsion

$$M = \frac{\mu\tau\pi a^2 b^2}{a^2 + b^2} \quad \text{and} \quad M_0 = \frac{\mu\tau\pi a^2 b^2}{2},$$

$$\frac{M}{M_0} = \frac{2ab}{a^2 + b^2} = \tanh 2\alpha, \quad \text{if } b/a = \tanh \alpha.$$

Hence we have, for the full ellipse

	$\alpha = \pi/6.$	$\alpha = \pi/3.$	$\alpha = \pi/2.$	$\alpha = 2\pi/3.$
M/M_0	·7807	·9701	·9963	·9995

If we compare this with the previous table, we see that for the flattest ellipse, $\alpha = \pi/6$, the ratio of the torsional rigidity to the torsional rigidity of the circular section of equal area, which I propose to call for brevity the *relative torsional rigidity*, is greater for the truncated than for the full ellipse, except in the last case, $\beta = \pi/2$. This last must necessarily be, since the strength of the section should be reduced by cutting two slits into it along the major axis. For the higher values of α we see that the relative torsional rigidity is always greater for the full than for the truncated ellipse.

§ 11. *Values of the Stresses at the Points of Symmetry.*

Passing now to the values of the stress, the values of $S_B/\mu\tau c$ are given, for the sixteen symmetrical sections, in the table below.

TABLE of $S_B/\mu\tau c$.

	$\beta = \pi/6.$	$\beta = \pi/4.$	$\beta = \pi/3.$	$\beta = \pi/2.$
$\alpha = \pi/6$	·7594	·8421	·8949	∞
$\alpha = \pi/3$	1·1482	1·6735	2·2690	∞
$\alpha = \pi/2$	1·3084	2·2798	3·6780	∞
$\alpha = 2\pi/3$	1·3897	2·7955	5·2484	∞

The values of $S_A/\mu\tau c$ were only calculated for $\beta = \pi/6$ and $\beta = \pi/4$, it being clear that for the given values of α , S_A would be less than S_B for $\beta = \pi/3$. The values of $S_A/(\mu\tau c)$ are given in the following table:—

TABLE of $S_A/\mu\tau c$.

	$\beta = \pi/6.$	$\pi/4.$
$\alpha = \pi/6$	·6730	·8126
$\alpha = \pi/3$	·8394	1·0975
$\alpha = \pi/2$	1·1971	1·5176
$\alpha = 2\pi/3$	1·8987	2·3650

The values of $S_A/\mu\tau c$, as calculated from the formula (21) above, actually turn out to be negative. The sign is, however, of no importance.

Several important results are seen to follow at once from these tables.

In the first place, when a keyway cut into a shaft of elliptic cross-section reduces to a mere slit, the stress at the inner extremity of the keyway is seen to be infinite, although this keyway is the limit of a single continuous curve and not of two curves making a sharp angle, as is the case for a slit along a radius of a circle, obtained as the limit of a keyway of the shape of a sector of the circle.

Such slits are thus bound to produce rupture or plastic flow of the material at their deepest points, whatever be the manner in which we approximate to them in practice.

The second point of importance, which these tables bring out clearly, is that the maximum strain and stress do not always occur, as most of the results obtained by DE SAINT-VENANT would lead one to suppose, and as THOMSON and TAIT ('Natural Philosophy,' vol. 1, Part II., § 710), and BOUSSINESQ ('Journal de Mathématiques,' Série II., vol. 16, p. 200) assumed, at the point of the boundary nearest the centre.

Indeed SAINT-VENANT himself, in his edition of NAVIER'S 'Leçons de Mécanique' (§ 33, p. 313), has given an example to the contrary, and it happens that the section dealt with in this example is closely analogous to the sections of fig. 2 in this paper. The shape of the section is reproduced in fig. 11 (p. 342), from SAINT-VENANT'S 'Leçons de NAVIER.' He calls it a "*section en double spatule analogue à celle d'un rail de chemin de fer.*" He gives two numerical examples in which the ratio of breadth to length of the section is '20 and '14, corresponding for our sections, when $\beta = \pi/6$, to $\alpha = 1.647$ and $\alpha = 1.985$ respectively. He finds in these two cases that the fail-points are *not* at the point of symmetry on the contour which is closest to the centre, but at points on the contour at a distance from the axis of symmetry of '46 and '52 of the half-length respectively.

Now it is easy to see from the tables above that the result which one would expect according to the ordinary rule, namely $S_B > S_A$, does hold in fifteen out of the sixteen cases, but there is one exception in the case of the section $\alpha = 2\pi/3$, $\beta = \pi/6$, when the greater of the two stresses is found to occur at A, the point further from the centre.

I was much struck at first by this apparently solitary deviation from the rule, and was inclined to ascribe it to some error in the arithmetic.

In order to test this, I calculated the values of S_A and S_B for the neighbouring section, $\beta = \pi/6$, $\alpha = 3\pi/4$. I found

$$\frac{S_A}{\mu\tau c} = 2.4333, \quad \frac{S_B}{\mu\tau c} = 1.4144,$$

confirming the previous exception.

I then took the expressions (21) and (22) for S_A and S_B , and tried to determine the limits to which they tended, when α was made very great.

Clearly, when we look at the second of expressions (22), we see that the second term must ultimately become vanishingly small, provided $\pi\alpha/2\beta > 2\alpha$, or $\beta < \pi/4$. For such values of β , then, S_B tends to the definite limit $\mu\tau c \tan 2\beta \cos \beta$, i.e., for $\beta = \pi/6$, $S_B/\mu\tau c$ tends to the limit 1.5 for large values of α .

For values of $\beta > \pi/4$ it would seem that S_B increases numerically to an indefinite extent.

Consider now the second expression for S_A . Clearly, if α exceed a certain value, $\tanh \frac{2n+1\pi\alpha}{2\beta}$ approximates so closely to unity that we may replace it in the series by unity, and the error will only be a small fraction of the series itself. We then find

$$\frac{S_A}{\mu\tau c} \text{ tends to } \sinh \alpha (\sec 2\beta - 1) - \frac{8\beta (\cosh 2\alpha + \cos 2\beta)}{\cosh \alpha} \sum_0^{\infty} \frac{(-1)^n}{\pi^2 (2n+1)^2 - 16\beta^2},$$

when α is large.

Substituting $\beta = \pi/6$, and using the Euler-Maclaurin sum-formula to calculate the series, I find

$$\left(\frac{S_A}{\mu\tau c} \right)_{\substack{\beta=\pi/6 \\ \alpha \text{ large}}} = \sinh \alpha - \frac{12}{\pi} \frac{(\cosh 2\alpha + \frac{1}{2})}{\cosh \alpha} (.190086),$$

and remembering that

$$\frac{\cosh 2\alpha + \frac{1}{2}}{\cosh \alpha} = 2 \cosh \alpha - \frac{1}{2 \cosh \alpha} = 2 \cosh \alpha, \text{ if } \alpha \text{ large,}$$

$$\sinh \alpha = \cosh \alpha - \frac{1}{\cosh \alpha + \sinh \alpha} = \cosh \alpha, \text{ if } \alpha \text{ large,}$$

we see that, when α is large,

$$\left(\frac{S_A}{\mu\tau c} \right)_{\beta=\pi/6} = -\cosh \alpha (.452147),$$

and, therefore, increases numerically indefinitely.

On the other hand, if α be very small, we get a flat section, A being now the point nearest to the centre. Looking at expressions (21) and (22) we see easily that

$$\left(\frac{S_A}{\mu\tau c} \right) \text{ tends to } -2\alpha$$

and

$$\left(\frac{S_B}{\mu\tau c} \right) \text{ to } (1 - \operatorname{sech} 2\alpha) \sin \beta + \frac{16}{\pi^2} \alpha \cos \beta \sum_0^{\infty} \frac{(-1)^n}{(2n+1)^2},$$

or, neglecting squares of α compared with the first power,

$$\left(\frac{S_B}{\mu\tau c} \right)_{\alpha \text{ small}} = \frac{16}{\pi^2} \alpha \cos \beta \sum_0^{\infty} \frac{(-1)^n}{(2n+1)^2}.$$

Now $\sum_0^{\infty} \frac{(-1)^n}{(2n+1)^2}$ lies between 1 and 8/9, hence $\left(\frac{S_B}{\mu\tau c} \right) < \left(\frac{16}{\pi^2} \cos \beta \right) \alpha$,

and $\frac{16}{\pi^2} \cos \beta$ being always < 2 , S_A is always numerically greater than S_B for small values of α . This confirms the usual rule, which we should expect, since the section approximates in this case to a flat rectangular section.

§ 12. Discussion of the Variations in these Stresses.

The variations in the stresses S_A , S_B are shown in fig. 9 (p. 340). This figure gives, not the values of the stresses themselves, but the ratio of the stresses to the maximum stress S_0 in the circular section of equal area. This ratio is plotted as ordinate to the various values of α as abscissæ. Of course, S_A , as given by the expressions (21) being negative throughout, the curve shows the ratio $(-S_A/S_0)$ and not S_A/S_0 .

The diagram is comparatively rough, especially near the origin, owing to the very limited number of points which I could calculate. The value of β selected was $\beta = \pi/6$.

When α is small, it is not difficult to show that, for $\beta = \pi/6$

$$S_B/S_0 = 1.799 \times \sqrt{\alpha}, \quad S_A/S_0 = -2.563 \times \sqrt{\alpha},$$

and when α is large

$$S_B/S_0 = 5.196e^{-\alpha}, \quad S_A/S_0 = -.7831.$$

These last enable us to see the form of the curves near the origin and at a great distance from it. They are perpendicular to the axis of α at the origin, and at first the curve of S_B lies below that of S_A . At some point between $\alpha = 0$ and $\alpha = .5$ they cross. This corresponds to the case of the square for rectangular cross-sections. S_A is now less than S_B , but instead of its remaining so, as we should have expected, the curves cross again near the value of $\alpha = 1.7$. The curve of S_A/S_0 now tends to become practically a straight line parallel to the axis, at a distance .7831 from it, and the curve of S_B/S_0 approaches the axis asymptotically.

The values of S_A/S_0 , S_B/S_0 are given in the tables below.

TABLE of S_A/S_0 .

	$\beta = \pi/6.$	$\beta = \pi/4.$
$\alpha = \pi/6$	1.1334	1.1741
$\alpha = \pi/3$.8589	.9506
$\alpha = \pi/2$.7796	.8246
$\alpha = 2\pi/3$.7706	.7924
$\alpha = 3\pi/4$.7724	
$\alpha = \infty$.7831	

TABLE of S_B/S_0 .

	$\beta = \pi/6$.	$\beta = \pi/4$.	$\beta = \pi/3$.
$\alpha = \pi/6$	1.2790	1.2168	1.1950
$\alpha = \pi/3$	1.1749	1.4494	1.7819
$\alpha = \pi/2$.8521	1.2388	1.7773
$\alpha = 2\pi/3$.5640	.9366	1.2928
$\alpha = 3\pi/4$.4490		

§ 13. Investigation of the Fail-Points other than the Points of Symmetry.

The question now arises, are A and B really points of *maximum slide*, and therefore shear? Assuming that the fail-points do occur on the contour, are we sure that there are not other points on the boundary where greater maxima occur, and may we not be in presence of a case like that of SAINT-VENANT'S *section en double spatule*.

To see whether this is so, it is necessary to go at some length into the equations determining the maximum stress.

Consider first the sides of the section $\eta = \pm \beta$. It is clear that the resultant stress along this side will be simply the component parallel to the contour, since the normal component must vanish in virtue of the boundary conditions. Calling S this resultant stress, we find easily

$$S = \frac{\mu}{c\sqrt{J}} \left(\frac{dw}{d\xi} + \frac{1}{2}\tau c^2 \sin 2\eta \right),$$

where

$$J = \frac{1}{2} (\cosh 2\xi + \cos 2\eta).$$

Hence we have to make

$$\left(\frac{Sc}{\mu} \right)^2 = \frac{1}{J} \left[\left(\frac{dw}{d\xi} \right)_{\eta=\beta} + \frac{1}{2}\tau c^2 \sin 2\beta \right]^2,$$

a maximum with regard to ξ .

We have therefore

$$\frac{d}{d\xi} \left(\frac{1}{J} \left\{ \frac{dw}{d\xi} + \frac{1}{2}\tau c^2 \sin 2\beta \right\}^2 \right) = 0,$$

that is

$$\frac{1}{J} \left(\frac{dw}{d\xi} + \frac{1}{2}\tau c^2 \sin 2\beta \right) \left[2 \frac{d^2 w}{d\xi^2} - \frac{1}{J} \frac{dJ}{d\xi} \left(\frac{dw}{d\xi} + \frac{1}{2}\tau c^2 \sin 2\beta \right) \right] = 0,$$

Take now the second value of w as given by (17), and we get

$$2 \frac{d^2 w}{d\xi^2} - \frac{1}{J} \frac{dJ}{d\xi} \left(\frac{dw}{d\xi} + \frac{1}{2} \tau c^2 \sin 2\beta \right) = \tau c^2 \sinh 2\xi \tan 2\beta - 8\tau c^2 (\cosh 2\alpha + \cos 2\beta)$$

$$\times \sum_{n=0}^{\infty} \left\{ \frac{(2n+1)\pi}{(2n+1)^2 \pi^2 - 16\beta^2} \frac{\sinh \frac{2n+1\pi\xi}{2\beta}}{\cosh \frac{2n+1\pi\alpha}{2\beta}} - \frac{2\beta \sinh 2\xi}{\cosh 2\xi + \cos 2\beta} \frac{\cosh \frac{2n+1\pi\xi}{2\beta}}{[2n+1]^2 \pi^2 - 16\beta^2} \frac{\cosh \frac{2n+1\pi\alpha}{2\beta}}{\cosh \frac{2n+1\pi\alpha}{2\beta}} \right\}.$$

Hence the equation giving the maxima and minima is

$$\tan 2\beta \sinh 2\xi$$

$$= 4 \frac{(\cosh 2\alpha + \cos 2\beta) (\cosh 2\xi + 2 \cos 2\beta)}{\cosh 2\xi + \cos 2\beta} \sum_{n=0}^{\infty} \frac{(2n+1)\pi}{(2n+1)^2 \pi^2 - 16\beta^2} \frac{\sinh \frac{2n+1\pi\xi}{2\beta}}{\cosh \frac{2n+1\pi\alpha}{2\beta}}$$

$$+ \frac{2(\cosh 2\alpha + \cos 2\beta)}{\cosh 2\xi + \cos 2\beta} \sum_{n=0}^{\infty} \left\{ \frac{\sinh [2n+1\pi + 4\beta] \frac{\xi}{2\beta}}{(2n+1)\pi + 4\beta} + \frac{\sinh [2n+1\pi - 4\beta] \frac{\xi}{\beta}}{(2n+1)\pi - 4\beta} \right\} \operatorname{sech} \frac{2n+1\pi\alpha}{2\beta}.$$

One root of this equation is $\xi = 0$. Now it is clear that since S^2 is zero, and therefore a minimum at $\xi = \alpha$, if it be not a maximum at $\xi = 0$, then there must be a maximum somewhere between $\xi = 0$ and $\xi = \alpha$.

To find whether $\xi = 0$ is a maximum or not, we have to investigate the sign of

$$\left[\frac{d^2}{d\xi^2} \left(\frac{1}{J} \left\{ \frac{dw}{d\xi} + \frac{1}{2} \tau c^2 \sin 2\beta \right\}^2 \right) \right]_{\xi=0, \eta=\beta},$$

i.e., we have to investigate the sign of

$$\frac{1}{J} \left(\frac{dw}{d\xi} + \frac{1}{2} \tau c^2 \sin 2\beta \right) \frac{d}{d\xi} \left[2 \frac{d^2 w}{d\xi^2} - \frac{1}{J} \frac{dJ}{d\xi} \left(\frac{dw}{d\xi} + \frac{1}{2} \tau c^2 \sin 2\beta \right) \right],$$

all the other terms vanishing when $\xi = 0$.

Now $\frac{1}{J} \left(\frac{dw}{d\xi} + \frac{1}{2} \tau c^2 \sin 2\beta \right)$ being always positive, we have to investigate the sign of

$$\frac{d}{d\xi} \left[2 \frac{d^2 w}{d\xi^2} - \frac{1}{J} \frac{dJ}{d\xi} \left(\frac{dw}{d\xi} + \frac{1}{2} \tau c^2 \sin 2\beta \right) \right] \text{ when } \xi = 0,$$

and therefore ultimately the sign of

$$E = \beta \tan 2\beta - \frac{(\cosh 2\alpha + \cos 2\beta)(1 + 2 \cos 2\beta)}{1 + \cos 2\beta} \sum_{n=0}^{\infty} \frac{(2n+1)^2 \pi^2}{(2n+1)^2 \pi^2 - 16\beta^2} \operatorname{sech} \frac{2n+1\pi\alpha}{2\beta} \\ - \frac{\cosh 2\alpha + \cos 2\beta}{1 + \cos 2\beta} \sum_{n=0}^{\infty} \operatorname{sech} \frac{2n+1\pi\alpha}{2\beta}.$$

I may remark here that all these differentiations are permissible, provided that ξ be less than α by a *finite amount*, however small, the series being then uniformly convergent. We may not, therefore, make α actually zero in the last expression. If, however, α is small but finite, then it is easy to see that E must be negative if $\beta < \pi/4$. Also if $\beta < \pi/4$, E algebraically increases continuously, until for a certain value α_0 of α it reaches the value zero. For all higher values of α it remains steadily positive.

§ 14. Critical Values of α and β .

It follows, therefore, that in all sections for which $\beta < \pi/4$, the maximum stress along the sides $\eta = \pm \beta$ occurs at the point B, until a certain critical value, $\alpha = \alpha_0$, is reached, when the stress at B becomes a minimum, and we now have two points of maximum stress on either side of B.

When $\beta = \pi/4$, E is apparently infinite, but it really tends to a finite limit. If we put $\beta = \pi/4 - \epsilon$ where ϵ will ultimately be made very small, and neglect terms in ϵ , ϵ^2 , &c., we find that the expression becomes

$$\frac{\pi}{8\epsilon} - \frac{1}{2} - 2 \cosh 2\alpha \sum_{n=0}^{\infty} \operatorname{sech} \frac{2n+1}{2} 2\alpha - \cosh 2\alpha \sum_{n=1}^{\infty} \operatorname{sech} (2n+1) 2\alpha + \frac{1}{4} \\ - (\cosh 2\alpha + 2\epsilon)(1 + 2\epsilon) \left(\frac{\pi}{2} - 2\epsilon \right) \frac{1}{4\epsilon} \operatorname{sech} \left\{ 2\alpha \left(1 + \frac{4\epsilon}{\pi} \right) \right\} \\ = - \frac{\pi}{4} - \frac{\pi}{4} \operatorname{sech} 2\alpha + \alpha \tanh 2\alpha - \frac{7}{\pi} - 3 \cosh 2\alpha \sum_{n=1}^{\infty} \operatorname{sech} (2n+1) 2\alpha.$$

When α is very great, this will ultimately be positive. Hence, here also we shall have a critical value α_0 . This value, however, is easily seen to lie outside the values of α taken in this paper.

I have not investigated so carefully the cases when $\beta > \pi/4$, as, for the particular sections selected, the maximum stress certainly occurs at B.

One point, however, is clear. When α is very large, the second and third terms settle the sign of E . The sign of these terms, again, is settled by the sign of the leading terms. E is negative if

$$1 + (1 + 2 \cos 2\beta) \frac{\pi^2}{\pi^2 - 16\beta^2}$$

is positive, i.e., if

$$\frac{\cos^2 \beta}{4\beta^2} + \frac{1 + 2 \cos 2\beta}{\pi^2 - 16\beta^2} > 0.$$

This will always be the case, provided β be greater than the root of the equation

$$\frac{2\beta}{\pi} = \cos \beta.$$

This root is $53^\circ 31'$ nearly.

Hence, for values of $\beta > 53^\circ 31'$ the maximum stress always occurs at the thinnest point of the section. This is the case for the sections of fig. 4 with broad keyways, for which $\beta = 60^\circ$.

Returning to the case of sections for which $\beta < \pi/4$ we have α_0 given by the equation

$$\beta \tan 2\beta = (\cosh 2\alpha_0 + \cos 2\beta) \left[2 \sum_{n=0}^{\infty} \operatorname{sech} \frac{2n+1}{2\beta} \alpha_0 + \frac{16\beta^2(1+\cos 2\beta)}{1+\cos 2\beta} \sum_{n=0}^{\infty} \frac{\operatorname{sech} \frac{2n+1}{2\beta} \alpha_0}{2n+1} \right].$$

Putting $\beta = \pi/6$ in this we have for the transcendental equation giving α_0 in this case

$$\frac{\pi}{2\sqrt{3}} = (\cosh 2\alpha_0 + \frac{1}{2}) \left[2 \sum_{n=0}^{\infty} \operatorname{sech} [2n+1] 3\alpha_0 + \frac{16}{3} \sum_{n=0}^{\infty} \frac{\operatorname{sech} [2n+1] 3\alpha_0}{(6n+1)(6n+5)} \right].$$

Now, for fairly large values of α_0 , we may neglect all terms in this summation except the first. We then have

$$\frac{\pi}{2\sqrt{3}} = \frac{23}{15} \frac{2 \cosh 2\alpha_0 + 1}{\cosh 3\alpha_0} = \frac{23}{15} (\operatorname{sech} \alpha_0 + 2 \operatorname{sech} 3\alpha_0)$$

whence I find $\alpha_0 = 1.225$.

Hence for values of α greater than this the maximum occurs at certain points on the contour, given by previously obtained equation in ξ .

§ 15. Calculation of the Position of Fail-Points and the Magnitude of the Maximum Stress for the Sections $\beta = \pi/6$, $\alpha = \pi/2$ and $\beta = \pi/6$, $\alpha = 2\pi/3$.

We have, therefore, if we wish to find the maximum stress for the sections $\alpha = \pi/2$ and $\alpha = 2\pi/3$ when $\beta = \pi/6$, to solve this transcendental equation :

$$\frac{\pi\sqrt{3}}{6} \frac{\sinh 2\xi (2 \cosh 2\xi + 1)}{2 \cosh 2\xi + 1} = 6 (\cosh 2\xi + 1) \sum_{n=0}^{\infty} \frac{2n+1}{(6n+1)(6n+5)} \frac{\sinh (6n+3)\xi}{\cosh (6n+3)\alpha} \\ + \sum_{n=0}^{\infty} \left\{ \frac{\sinh (6n+5)\xi}{6n+5} + \frac{\sinh (6n+1)\xi}{6n+1} \right\} \frac{1}{\cosh (6n+3)\alpha}$$

which may be put into the slightly simpler form

$$\frac{\pi\sqrt{3}}{6 (\cosh 2\xi + \frac{1}{2})} = \frac{12 \cosh \xi}{\sinh 3\xi} \sum_{n=0}^{\infty} \frac{(2n+1)}{(6n+1)(6n+5)} \frac{\sinh (6n+3)\xi}{\cosh (6n+3)\alpha} \\ + \frac{1}{\cosh \xi \sinh 3\xi} \sum_{n=0}^{\infty} \left\{ \frac{\sinh (6n+5)\xi}{(6n+5) \cosh (6n+3)\alpha} + \frac{\sinh (6n+1)\xi}{(6n+1) \cosh (6n+3)\alpha} \right\}.$$

I find the roots of this to be approximately given by

$$\xi = 1.475 \text{ when } \alpha = 2\pi/3,$$

$$\xi = .821 \text{ when } \alpha = \pi/2.$$

The corresponding values of $S/\mu\tau c$ are found to be 2.1084 and 1.4041 respectively. Comparing these with the values of $S_A/\mu\tau c$ given on p. 331, we see that the values of the stresses corresponding to the maximum on the broad side are the greater, and hence we have really a case absolutely analogous to SAINT-VENANT'S *section en double spatule*, with four fail-points symmetrically distributed, all of them lying on the broad sides of the contour.

§ 16. Case where α is made very great.

It is interesting to see to what limit the fail-points tend, when α is made very great. We have

$$\frac{S}{\mu\tau c} = \frac{1}{\sqrt{J}} \left[\frac{1}{2} \tan 2\beta (\cosh 2\xi + \cos 2\beta) - 8\beta (\cosh 2\alpha + \cos 2\beta) \sum_{n=0}^{\infty} \frac{\cosh \frac{2n+1\pi\xi}{2\beta}}{\left[(2n+1)^2\pi^2 - 16\beta^2 \right] \cosh \frac{2n+1\pi\alpha}{2\beta}} \right].$$

Replace now $\frac{1}{2} \tan 2\beta$ by its equivalent $8\beta \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2\pi^2 - 16\beta^2}$.

$$\frac{S}{\mu\tau c} = \frac{8\beta}{\sqrt{J}} \sum_{n=0}^{\infty} \frac{\left\{ (\cosh 2\xi + \cos 2\beta) - (\cosh 2\alpha + \cos 2\beta) - \frac{\cosh \frac{2n+1\pi\xi}{2\beta}}{\cosh \frac{2n+1\pi\alpha}{2\beta}} \right\}}{(2n+1)^2\pi^2 - 16\beta^2}.$$

Now if ξ, α be great, we have $\cosh = \frac{1}{2} (\exp.)$ approximately. Hence, if we suppose $\xi = \alpha - \theta$ where θ is finite, so that we are dealing with points whose distances from the centre bear a finite ratio to the dimensions of the section, we find

$$\frac{S}{\mu\tau c} = 8\beta e^\alpha \sum_{n=0}^{\infty} \frac{e^{-\theta} - e^{\theta \left(1 - \frac{2n+1\pi}{2\beta}\right)}}{(2n+1)^2\pi^2 - 16\beta^2}$$

+ terms negligible in comparison and ultimately vanishingly small when α is made infinite.

Hence we have to make

$$\sum_{n=0}^{\infty} \frac{e^{-\theta} - e^{\theta \left(1 - \frac{(2n+1)\pi}{2\beta}\right)}}{(2n+1)^2\pi^2 - 16\beta^2}$$

a maximum.

Differentiating, the series being absolutely and uniformly convergent, we get

$$2 \times 2$$

$$e^{-\theta} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2 \pi^2 - 16\beta^2} - \sum_{n=0}^{\infty} \frac{\left(\frac{2n+1}{2} \pi - 1 \right) e^{\theta \left(1 - \frac{(2n+1)\pi}{2\beta} \right)}}{(2n+1)^2 \pi^2 - 16\beta^2} = 0,$$

i.e.,

$$\frac{\tan 2\beta}{8} = \sum_{n=0}^{\infty} \frac{(2n+1)\pi - 2\beta}{(2n+1)^2 \pi^2 - 16\beta^2} e^{\theta \left(1 - \frac{(2n+1)\pi}{2\beta} \right)}.$$

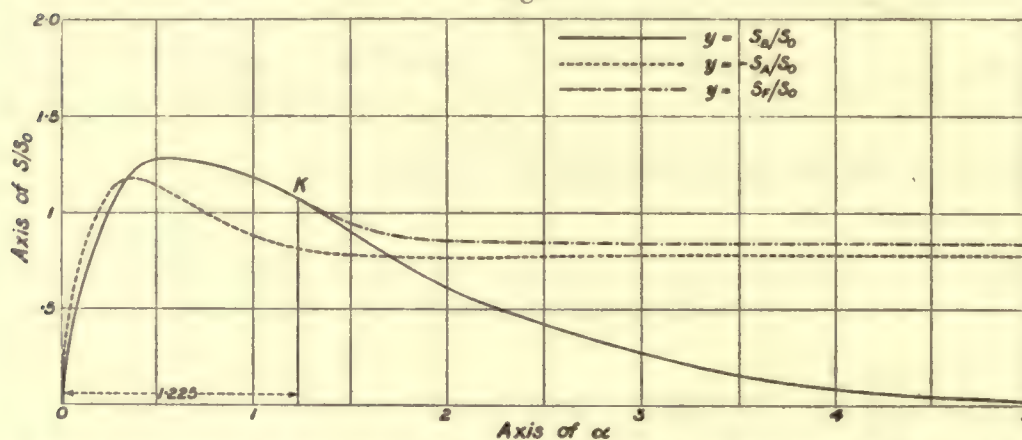
This is the equation giving θ . When we put in it $\beta = \pi/6$

$$\frac{\pi}{16\sqrt{3}} = \sum_{n=0}^{\infty} \frac{3n+1}{(6n+1)(6n+5)} e^{-(6n+1)\theta}.$$

I find from this $\theta = .577$ approximately, and the corresponding value of $S/\mu\tau c = .48984 \cosh \alpha$. Referring to the value of $S_A/\mu\tau c$ given on p. 333, we see that the real fail-point is on the broader side.

The curve of true maximum stress \bar{S}/S_0 is shown also in fig. 9. It joins on to the

Fig. 9.



Showing the variation in the value of S/S_0 as α increases, at the three points A, B, F, of Fig. 2.
 $\beta = \text{const.} = \pi/6.$

curve of S_B/S_0 at the point corresponding to the value $\alpha = 1.225$. It then remains above the curve of S_A/S_0 , tending ultimately to a straight line parallel to the axis, at a height .8484 above it.

§ 17. Proof that there can be no other Maxima.

It remains to show that the point $\eta = 0$ corresponds to a maximum along the side $\xi = \alpha$, and also that there is no maximum of the resultant stress inside the section.

The stress S along $\xi = \alpha$ is given by

$$\left(\frac{Sc}{\mu} \right)^2 = \frac{1}{J} \left(\frac{dw}{d\eta} - \frac{1}{2} \tau c^2 \sinh 2\alpha \right)_{\xi=\alpha}^2.$$

The equation giving the maxima or minima is found as before. It is

$$\left[2 \frac{d^2 w}{d\eta^2} - \frac{1}{J} \frac{dJ}{d\eta} \left(\frac{dw}{d\eta} - \frac{1}{2} \tau c^2 \sinh 2\alpha \right) \right]_{\eta=\alpha} = 0,$$

or, using the *first* of expressions (17) for w

$$\begin{aligned} \sin 2\eta \tanh 2\alpha + 8 (\cosh 2\alpha + \cos 2\beta) \sum_{n=0}^{\infty} \frac{\sinh \frac{(2n+1)\pi\eta}{2\alpha}}{\cosh \frac{(2n+1)\pi\beta}{2\alpha}} \frac{(2n+1)\pi}{(2n+1)^2\pi^2 + 16\alpha^2} \\ + \frac{16\alpha \sin 2\eta (\cosh 2\alpha + \cos 2\beta)}{\cosh 2\alpha + \cos 2\eta} \sum_{n=0}^{\infty} \frac{\cosh \frac{2n+1\pi\eta}{2\alpha}}{(2n+1)^2\pi^2 + 16\alpha} \frac{1}{\cosh \frac{2n+1\pi\beta}{2\alpha}} = 0. \end{aligned}$$

The left-hand side is always positive. Hence there is no root except $\eta = 0$, and that corresponds to a maximum.

That no absolute *maximum* can exist inside the section can be proved as follows:—

We have

$$\widehat{xz}/\mu = dw/dx - \tau y, \quad \widehat{yz}/\mu = dw/dy + \tau x.$$

Suppose at any point P inside the section $S^2 = \widehat{xz}^2 + \widehat{yz}^2$ is a maximum. The above forms for $\widehat{xz} + \widehat{yz}$ being independent of axes, let us take for axes of x and y the direction of the resultant stress across the section at P and the perpendicular to it. So that $\widehat{yz} = 0$ at P.

Consider a near point P'. Let \widehat{xz}' , \widehat{yz}' be the stresses at P'. Then, since S^2 is a maximum at P,

$$\widehat{xz}^2 > \widehat{xz}'^2 + \widehat{yz}'^2,$$

but

$$yz'^2 > 0.$$

Therefore

$$xz'^2 > xz'^2,$$

or \widehat{xz} is a numerical maximum.

But since

$$d^2 w/dx^2 + d^2 w/dy^2 = 0,$$

therefore also

$$\frac{d^2(\widehat{xz})}{dx^2} + \frac{d^2(\widehat{xz})}{dy^2} = 0;$$

and it is well known that no function can have an absolute maximum or an absolute minimum inside a region where it satisfies LAPLACE'S equation. This is in fact a particular case of the general theorem that a potential cannot have a maximum in free space.

Hence we have proved that the only fail-points are those which we have already investigated.

§ 18. *Deductions from the above and Criticism of BOUSSINESQ'S Proof of the Position of Fail-Points.*

Thus we see the study of these symmetrical sections is extremely instructive as regards the position of the fail-points. They show us the connection between the rectangular section and the section with a neck, and they give us the limiting cases, when the four fail-points coalesce into two, and *vice versa*. The four fail-points begin to occur after the ratio of the long to the short axis of the section exceeds a certain value, which depends upon the angle of the bounding hyperbolas. As the indented appearance of the section becomes more obvious, that is, as β increases, this limiting value becomes greater and greater until, when the angle between the asymptotes is less than 73° the fail-point is always at the vertex of the hyperbolas. But in no case are the fail-points on the convex sides of the sections, unless the ellipses are so flat that the points A are nearer to the centre than the points B.

M. BOUSSINESQ has given ('Journal de Mathématiques,' Série II., vol. 16, p. 200) a sketch of a proof that the fail-points must be sought for "sur les petits diamètres

Fig. 10.

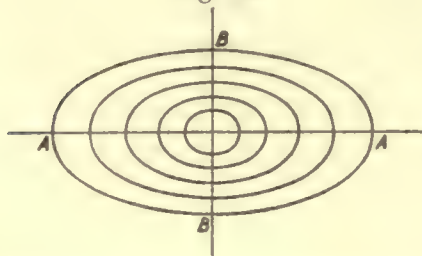
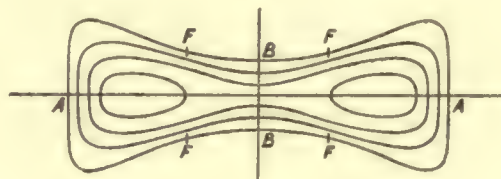


Fig. 11.



des sections." As this statement is in opposition with the results of the present paper and with DE SAINT-VENANT'S results for the rail sections already mentioned, I venture to suggest that M. BOUSSINESQ'S reasoning hardly holds in the case of sections part of whose contour is convex and part concave, for the following reason. The problem of torsion is mathematically analogous to that of a cylindrical vortex of uniform strength, whose cross-section is that of the shaft considered. The motion being in two dimensions we have a stream function ψ , and the resultant stress at any point in the torsion problem is the same as $d\psi/dn$ in the hydrodynamical analogy, dn being an element of the normal to any stream-line.

Now if we draw the stream-lines for equidistant values of ψ , they will, says M. BOUSSINESQ, "reproduce the irregularities of the contour, but more and more faintly, so that the curves are spaced at greater intervals along the large, then along the small diameters." In consequence, $d\psi/dn$, or the stress, is greater in the latter case. The above argument assumes that the same number of stream-lines cross each

diameter. This will undoubtedly be the case, and M. BOUSSINESQ's proof will hold, if the boundary of the section be everywhere convex, for then it is evident that each stream-line will consist of a single simple oval (fig. 10). But when we deal with sections like those of the present paper it is by no means so clear that this will be the case. There may be stream-lines which consist of two separate ovals (see fig. 11), and it then becomes very much open to question towards which part of the section the lines will be most crowded. In fact in some cases, as we have seen, this will occur at intermediate points, F (fig. 11), and in other cases the narrowness of the neck or the sharpness of the bend will counterbalance the limited number of the stream-lines through the neck, and the fail-points will be at B, B.

§ 19. *Comparison with SAINT-VENANT'S Results. "Efficiency" of the various Sections.*

When we compare the results given by these sections bounded by confocal ellipses and hyperbolas with those given by DE SAINT-VENANT in his edition of the 'Leçons de NAVIER' for the "sections en double spatule," we find very good agreement. Thus the critical value of the ratio of breadth of neck to length for which the fail-points split up each into two is given by SAINT-VENANT as '3247. For the sections of this paper, when $\beta = \pi/6$, I find this critical value to be '3215.

The following are the principal numerical points (see 'Leçons de NAVIER,' p. 365) :—

	Section $\alpha = \pi/2, \beta = \pi/6.$	SAINT-VENANT'S section, $c/b = .20.$
Ratio of breadth of neck to length2173	.20
M/M_04443	.3921
S/S_0 (S being maximum stress)9144	.8668
$E = (M/M_0)/(S/S_0)$4859	.4524
Ratio of distance of fail-points from short axis to length of longer semi-axis3449	.4561

	Section $\alpha = 2\pi/3, \beta = \pi/6.$	SAINT-VENANT'S section, $c/b = .14.$
Ratio of breadth of neck to length1250	.14
M/M_03955	.3465
S/S_08557	.8226
E4622	.4212
Ratio of distance of fail-points from short axis to length of longer semi-axis4486	.523

On the whole the sections of the present paper appear the more useful, M/M_0 and the quantity E being greater than for DE SAINT-VENANT'S rail sections. This

quantity $E I$ I propose to call the "efficiency" or "usefulness" of the shaft. It is equal to $(S_0/M_0)/(S/M)$, and gives us the ratio of maximum stress to torsional rigidity, compared with the same ratio for the circle of equal area, that is, it gives us a measure of how much torsion we may put into the shaft without impairing its elasticity. Thus if M be the maximum torsion moment which the given shaft will bear without failure of elasticity, M_0 the maximum torsion moment which the shaft of equal circular section (made of the same material) will stand, then the corresponding stresses, S, S_0 are each equal to the limiting elastic stress of the material and

$$M/M_0 = \text{efficiency} = E,$$

or the limiting torsion moment of a shaft of any section is obtained from that of the circular section of the same area by merely multiplying by the "efficiency" as thus defined.

TABLE of "Efficiency" of the sixteen given sections.

	$\beta = \pi/6.$	$\beta = \pi/4.$	$\beta = \pi/3.$	$\beta = \pi/2.$
$\alpha = \pi/6$	·6846	·7104	·6869	0
$\alpha = \pi/3$	·5206	·5022	·4376	0
$\alpha = \pi/2$	·4859	·4218	·3211	0
$\alpha = 2\pi/3$	·4622	·4643	·3550	0

A glance at the above suffices to show that the efficiency of these sections is, in general, about one-half, that is, on the whole, this form of shaft is about half as useful as the shaft of circular section. The zero efficiency in the case of the slit ($\beta = \pi/2$) is due to the infinite stress in the keyway.

§ 20. *Analysis for the Sections bounded by one Elliptic and one Hyperbolic Arc.*

I now pass on to the consideration of cross-sections, bounded by an ellipse and a single branch of a confocal hyperbola. Such sections are shown in figs. 6-8.

In this case we shall find it more convenient to define ξ and η by the equations

$$\left. \begin{aligned} x &= c \cosh \xi \cos \eta \\ y &= c \sinh \xi \sin \eta \end{aligned} \right\} \dots \dots \dots (23)$$

where $-\alpha < \xi < +\alpha, 0 < \eta < \beta$.

We find in the same way as before

$$dw/d\xi^2 + dw/d\eta^2 = 0.$$

$$\left. \begin{aligned} dw/d\xi + \frac{1}{2}\tau c^2 \sin 2\eta &= 0 & \xi = \pm \alpha, & 0 < \eta < \beta \\ dw/d\eta + \frac{1}{2}\tau c^2 \sinh 2\xi &= 0 & \eta = \beta, & -\alpha < \xi < +\alpha \end{aligned} \right\} \quad (24).$$

There is, however, in the present case, a further condition. For, referring to figs. 6-8, when we cross the line SB_1B_2 , S being that focus of the conics which is inside the section, η is continuous, passing through the value 0, but ξ is discontinuous and changes from positive to negative. We have to ensure that the function of ξ and η , which shall represent w , shall be continuous in crossing $\eta = 0$, and that its space-differential coefficients shall also be continuous. The latter condition implies that $dw/d\eta$ must change sign; this being so, all the conditions will be satisfied.

Let us write

$$w = -\frac{1}{4}\tau c^2 \frac{\sinh 2\xi \sin 2\eta}{\cosh 2\alpha} + w_1,$$

conditions (24) then become

$$\left. \begin{aligned} dw_1/d\xi &= 0 & \text{when } \xi = \pm \alpha, & 0 < \eta < \beta \\ \frac{dw_1}{d\eta} + \frac{1}{2}\tau c^2 \left(1 - \frac{\cos 2\beta}{\cosh 2\alpha}\right) \sinh 2\xi &= 0 & \text{when } \eta = \beta, & -\alpha < \xi < +\alpha \end{aligned} \right\} \quad (25).$$

If we now assume

$$w_1 = \sum_{n=0}^{\infty} A_n \sinh \frac{2n+1\pi\eta}{2\alpha} \cdot \sin \frac{2n+1\pi\xi}{2\alpha},$$

then the conditions of continuity and the first of (25) are identically satisfied.

A_n is found from the second equation of (25) in the same way as in § 4.

$$A_n = -\frac{16\tau c^2 \alpha^2 (-1)^n (\cosh 2\alpha - \cos 2\beta)}{\pi (2n+1) [\pi^2 (2n+1)^2 + 16\alpha^2] \cosh \frac{2n+1\pi\beta}{2\alpha}}.$$

And thus

$$\begin{aligned} w = & -\frac{1}{4}\tau c^2 \frac{\sinh 2\xi \sin 2\eta}{\cosh 2\alpha} - 16\tau c^2 \alpha^2 (\cosh 2\alpha - \cos 2\beta) \\ & \times \sum_{n=0}^{\infty} \frac{(-1)^n \sinh \frac{2n+1\pi\eta}{2\alpha} \sin \frac{2n+1\pi\xi}{2\alpha}}{(2n+1)\pi [\pi^2 (2n+1)^2 + 16\alpha^2] \cosh \frac{2n+1\pi\beta}{2\alpha}} \quad (26). \end{aligned}$$

The shears are given by the equations

$$\left. \begin{aligned} \frac{\widehat{yz}}{\mu} &= \frac{1}{cJ} \left(\sinh \xi \cos \eta \frac{dw_1}{d\xi} - \cosh \xi \sin \eta \frac{dw_1}{d\eta} \right) - \tau c \sinh \xi \sin \eta (1 + \operatorname{sech} 2\alpha) \\ \frac{\widehat{xz}}{\mu} &= \frac{1}{cJ} \left(\cosh \xi \sin \eta \frac{dw_1}{d\xi} + \sinh \xi \cos \eta \frac{dw_1}{d\eta} \right) + \tau c \cosh \xi \cos \eta (1 - \operatorname{sech} 2\alpha) \end{aligned} \right\} \quad (27),$$

where J now stands for the quantity

$$\cosh^2 \xi \sin^2 \eta + \sinh^2 \xi \cos^2 \eta.$$

The torsion moment M

$$\begin{aligned} &= \iint (x\widehat{yz} - y\widehat{xz}) dx dy \\ &= \mu \tau c^4 \int_0^\beta d\eta \int_{-\alpha}^\alpha d\xi \{ \cosh^2 \xi \cos^2 \eta (1 - \operatorname{sech} 2\alpha) + \sinh^2 \xi \sin^2 \eta (1 + \operatorname{sech} 2\alpha) \} J \\ &\quad + \frac{\mu c^2}{2} \int_0^\beta d\eta \int_{-\alpha}^\alpha d\xi \left(\sin 2\eta \frac{dw_1}{d\xi} + \sinh 2\xi \frac{dw_1}{d\eta} \right) \\ &= \frac{\mu \tau c^4}{8} \int_0^\beta d\eta \int_{-\alpha}^\alpha d\xi \left[(\cosh 4\xi - \cos 4\eta) - \operatorname{sech} 2\alpha (\cosh 2\xi - \cos 2\eta) \right. \\ &\quad \left. - \operatorname{sech} 2\alpha (\cosh 4\xi \cos 2\eta - \cosh 2\xi \cos 4\eta) \right] \\ &\quad + \frac{\mu c^2}{2} \int_0^\beta \left[w_1 \right]_{-\alpha}^\alpha \sin 2\eta d\eta + \frac{\mu c^2}{2} \int_{-\alpha}^\alpha \left[w_1 \right]_0^\beta \sinh 2\xi d\xi. \end{aligned}$$

When this is integrated out and reduced as before, it is found that

$$M = \frac{\mu \tau c^4}{16} \left\{ \begin{aligned} &(\beta \sinh 4\alpha - \alpha \sin 4\beta) \tanh^2 2\alpha \\ &+ 2 \sin 2\beta (2\alpha \operatorname{sech}^2 2\alpha - \tanh 2\alpha) (\cosh 2\alpha - \cos 2\beta) \\ &- 2048\alpha^4 (\cosh 2\alpha - \cos 2\beta)^2 \sum_{n=0}^{\infty} \frac{1}{\pi (2n+1)} \frac{\tanh \frac{(2n+1)\pi\beta}{2\alpha}}{[\pi^2 (2n+1)^2 + 16\alpha^2]^{\frac{1}{2}}} \end{aligned} \right\} \quad (28).$$

§ 21. *Alternative Solution for these Sections.*

For this type of section also we can find an alternative solution.

Suppose we assume

$$w = -\frac{1}{4} \tau c^2 \frac{\sinh 2\xi \sin 2\eta}{\cos 2\beta} + w_1.$$

These conditions (24) reduce to :

$$\left. \begin{aligned} \frac{dw_1}{d\xi} + \frac{1}{2} \tau c^2 \sin 2\eta \left(1 - \frac{\cosh 2\alpha}{\cos 2\beta} \right) &= 0, \quad \xi = \pm \alpha, \quad 0 < \eta < \beta \\ dw_1/d\eta &= 0 \quad \eta = \beta \quad -\alpha < \xi < \alpha \end{aligned} \right\} \quad \cdot \cdot \quad (29).$$

Also the condition of continuity requires that w_1 must be odd in η .

We assume, therefore,

$$w_1 = \sum_{n=0}^{\infty} A_n \sin \frac{2n+1\pi\eta}{2\beta} \sinh \frac{2n+1\pi\xi}{2\beta}.$$

But since

$$\sin 2\theta = a_1 \sin \frac{\pi\theta}{2\beta} + \dots + a_n \sin \frac{2n+1\pi\theta}{2\beta} + \dots$$

where

$$a_n = \frac{(-1)^n 16\beta \cos 2\beta}{(2n+1)^2 \pi^2 - 16\beta^2},$$

we find easily from the first equation of (29), comparing coefficients

$$A_n = \frac{(-1)^n 16\tau c^2 \beta^2 (\cosh 2\alpha - \cos 2\beta)}{(2n+1)\pi [2n+1]^2 \pi^2 - 16\beta^2} \cosh \frac{2n+1\pi\alpha}{2\beta},$$

and

$$w = -\frac{1}{4}\tau c^2 \frac{\sinh 2\xi \sin 2\eta}{\cos 2\beta} + 16\tau c^2 \beta^2 (\cosh 2\alpha - \cos 2\beta) \sum_{n=0}^{\infty} \frac{(-1)^n \sin \frac{2n+1\pi\eta}{2\beta} \sinh \frac{2n+1\pi\xi}{2\beta}}{(2n+1)\pi [2n+1]^2 \pi^2 - 16\beta^2} \cosh \frac{2n+1\pi\alpha}{2\beta} \quad (30).$$

The stresses and torsion moment are deduced without difficulty. They are :

$$\frac{\partial z}{\partial \mu} = -\tau c \sinh \xi \sin \eta (1 + \sec 2\beta) + 32\tau c \beta^2 \frac{(\cosh 2\alpha - \cos 2\beta)}{(\cosh 2\xi - \cos 2\eta)} \times \sum_{n=0}^{\infty} \frac{\left(\sinh \xi \cos \eta \frac{d}{d\xi} - \cosh \xi \sin \eta \frac{d}{d\eta} \right) (-1)^n \sin \frac{2n+1\pi\eta}{2\beta} \sinh \frac{2n+1\pi\xi}{2\beta}}{(2n+1)\pi [2n+1]^2 \pi^2 - 16\beta^2} \cosh \frac{2n+1\pi\alpha}{2\beta} \quad (31).$$

$$\frac{\partial z}{\partial \mu} = \tau c \cosh \xi \cos \eta (1 - \sec 2\beta) + 32\tau c \beta^2 \frac{(\cosh 2\alpha - \cos 2\beta)}{(\cosh 2\xi - \cos 2\eta)} \times \sum_{n=0}^{\infty} \frac{\left(\cosh \xi \sin \eta \frac{d}{d\xi} + \sinh \xi \cos \eta \frac{d}{d\eta} \right) (-1)^n \sin \frac{2n+1\pi\eta}{2\beta} \sinh \frac{2n+1\pi\xi}{2\beta}}{(2n+1)\pi [2n+1]^2 \pi^2 - 16\beta^2} \cosh \frac{2n+1\pi\alpha}{2\beta} \quad (32).$$

$$M = \frac{\mu \tau c^4}{16} \left[\begin{aligned} & -(\beta \sinh 4\alpha - \alpha \sin 4\beta) \tan^2 2\beta \\ & + 2 \sinh 2\alpha (\cosh 2\alpha - \cos 2\beta) (2\beta \sec^2 2\beta - \tan 2\beta) \\ & - 2048 \beta^4 (\cosh 2\alpha - \cos 2\beta)^2 \sum_{n=0}^{\infty} \frac{\tanh \frac{2n+1\pi\alpha}{2\beta}}{(2n+1)\pi [2n+1]^2 \pi^2 - 16\beta^2} \end{aligned} \right] \quad (33).$$

The same remarks which were made concerning the solution in § 5 apply here. The critical values are $\beta = \pi/4$, $\beta = 3\pi/4$. The limits to which the values of w , M and the stresses, given in (30)-(33), tend, are easily obtained if required. In practice, however, the other solution would probably be used.

§ 22. *Numerical Results. Effects of Keyways upon Torsional Rigidity.*

I have worked out numerically six cases of this type of section. The sections selected are shown in figs. 6-8. The bounding ellipses are $\alpha = \pi/6$ and $\alpha = \pi/2$, the bounding hyperbolas are $\beta = \pi/2$, $3\pi/4$ and π , giving respectively (a) the half ellipse, (b) the ellipse with a rectangular hyperbolic keyway, (c) the ellipse with a single thin keyway or slit.

The values of the torsion moment and of its ratio to the torsion moment of the equal circular section, are shown in the tables below.

TABLE of $M/\mu\tau c^4$.

	$\beta = \pi/2$.	$\beta = 3\pi/4$.	$\beta = \pi$.
$\alpha = \pi/6$	·1365	·3944	·4731
$\alpha = \pi/2$	10·354	26·319	40·142

TABLE of M/M_0 .

	$\beta = \pi/2$.	$\beta = 3\pi/4$.	$\beta = \pi$.
$\alpha = \pi/6$	·8907	·8244	·7718
$\alpha = \pi/2$	·7907	·7985	·7664

When we look at these results we see that the torsional rigidity of these sections is always less than that of the circular section. The sections consisting of a complete ellipse with one fine slit up to the focus are weaker than the half-ellipse or the sections with a broad keyway. This is more particularly shown in the case of the more elongated ellipse, $\alpha = \pi/6$.

With regard to the effects of slits, or thin keyways, it is interesting to compare the values of M/M_0 for the ellipses $\alpha = \pi/6$, $\alpha = \pi/2$, when (i.) there are no slits, (ii.) there is one slit, (iii.) there are two slits

We find

	$\alpha = \pi/6.$	$\alpha = \pi/2.$
(i.) $M/M_0 =$.7807	.9963
(ii.)7718	.7664
(iii.)7628	.5711

It follows that, in the first case, the cutting of one thin keyway lowers the rigidity of the section by 1.14 per cent., and of two keyways by 2.29 per cent. Hence the effect of two such keyways is slightly greater, if anything, than twice the effect of a single keyway, in the case of the more elongated ellipse. The difference is, however, practically negligible.

In the other case the result is different. The reduction of the torsional rigidity is very great: it amounts to 23.08 per cent. for one keyway and to 42.68 per cent. for two keyways. Here we see the effect of two keyways is rather less than twice the effect of one.

We may infer, however, from these two results that we may in practice, without very large error, if we have a number of keyways cut symmetrically into a section, and we know the effect on the torsional rigidity of any single keyway, assume that the effect of all the keyways is the sum of their separate effects.

Another important point which is brought out by the above results is that the effect of such a keyway upon the torsional rigidity is by no means simply proportional to the depth of the keyway, but increases according to some much more rapid law.

Thus, for the ellipse $\alpha = \pi/6$, the depth of the keyway = .123 (semi-major axis). For the ellipse $\alpha = \pi/2$, the depth = .601 (semi-major axis). Thus, when the depth of the keyway is only decreased to one-fifth of what it was before, the reduction of torsional rigidity falls from 23 per cent. to 1 per cent., or nearly in the ratio of the *squares* of the depths of the keyways.

This result may explain the fact that, when keyways of only moderate depth are cut into shafts, the decrease of torsional rigidity is by no means so great as would have been inferred from DE SAINT-VENANT'S results for a circular section, with a thin keyway or slit extending right up to the centre.

If we suppose, which appears reasonable, that the effect of such a slit upon an ellipse, which is not very elongated, does not differ much from the effect on a circle, we see that a keyway, whose depth equals about one-eighth of the radius, will decrease the torsional rigidity by only about 1 per cent.

Now, when we make $\alpha = \infty$, we get the case of the circle with a keyway going right up to the centre. The reduction of torsional rigidity is then 44 per cent. about.

Hence we have, roughly,

Depth of keyway in terms of radius.	Reduction of torsional rigidity.
	per cent.
1·00	44
·60	23
·12	1

If the reduction of torsional rigidity were simply proportional to the depth of the keyway, the last two results ought to be 26·4 per cent. and 5·3 per cent. respectively.

It may be objected to these deductions that in the above sections, the fact that the stress at the vertex of the keyway is infinite, violates the physical conditions assumed by the theory of elasticity and renders our results untrustworthy.

My answer to this is that these cases should really be considered as limiting cases. If, instead of considering a section where the keyway is actually a straight line, we consider a hyperbola with a very sharp bend, we can easily ensure, provided the angle of torsion be not too great, that the physical conditions shall *not* be violated, and, on the other hand, the values of the torsional rigidity (since they tend to a finite limit) will differ but little from the values obtained above. The very fact that the torsional rigidity tends to a finite limit shows that, even in the extreme case, the area where the physical considerations are violated is infinitesimal.

Finally, in drawing conclusions from such results we shall only be following the example of SAINT-VENANT and of THOMSON and TAIT, who have not hesitated to use results found in a precisely similar way for such keyways cut into a circle.

§ 23. *Values of the Stresses.*

I have also determined the stresses at three points on the boundary of the section, in order to find where the stress was greatest. The points selected are denoted in figs. 6, 7, and 8 by the letters A, B, C.

A is the vertex of the hyperbola, B is the point opposite to A, and C is the point corresponding to $\eta = \pi/2$, $\xi = \pm \alpha$.

A is given by $\xi = 0$, $\eta = \beta$, and B by $\xi = \pm \alpha$, $\eta = 0$.

If S_A , S_B , S_C denote the corresponding stresses, I find

$$\begin{aligned} \frac{S_A}{\mu\tau c} &= \cos \beta (1 - \operatorname{sech} 2\alpha) \\ &- \frac{8\alpha (\cosh 2\alpha - \cos 2\beta)}{\sin \beta} \sum_{n=0}^{\infty} \frac{(-1)^n \tanh \frac{2n+1\pi\beta}{2\alpha}}{\pi^2 (2n+1)^2 + 16\alpha^2} \\ &= -\tan 2\beta \sin \beta \\ &+ \frac{8\beta (\cosh 2\alpha - \cos 2\beta)}{\sin \beta} \sum_{n=0}^{\infty} \frac{\operatorname{sech} \frac{2n+1\pi\alpha}{2\beta}}{(2n+1)^2\pi^2 - 16\beta^2} \dots \dots \dots (34), \end{aligned}$$

$$\begin{aligned}
\frac{S_B}{\mu\tau c} &= \tanh 2\alpha \sinh \alpha \\
&\quad - \frac{8\alpha (\cosh 2\alpha - \cos 2\beta)}{\sinh \alpha} \sum_{n=0}^{\infty} \frac{\operatorname{sech} \frac{2n+1\pi\beta}{2\alpha}}{(2n+1)^2\pi^2 + 16\alpha^2} \\
&= -\cosh \alpha (\sec 2\beta - 1) \\
&\quad + \frac{8\beta (\cosh 2\alpha - \cos 2\beta)}{\sinh \alpha} \sum_{n=0}^{\infty} \frac{(-1)^n \tanh \frac{2n+1\pi\alpha}{2\beta}}{2n+1)^2\pi^2 - 16\beta^2} \dots \dots \dots (35),
\end{aligned}$$

$$\begin{aligned}
\frac{S_C}{\mu\tau c} &= -\sinh \alpha (1 + \operatorname{sech} 2\alpha) \\
&\quad + \frac{8\alpha (\cosh 2\alpha - \cos 2\beta)}{\cosh \alpha} \sum_{n=0}^{\infty} \frac{\cosh \frac{2n+1\pi^2}{4\alpha} / \cosh \frac{2n+1\pi\beta}{2\alpha}}{2n+1)^2\pi^2 + 16\alpha^2} \\
&= -\sinh \alpha (1 + \sec 2\beta) \\
&\quad - \frac{8\beta (\cosh 2\alpha - \cos 2\beta)}{\cosh \alpha} \sum_{n=0}^{\infty} \frac{(-1)^n \sin \frac{2n+1\pi^2}{4\beta} \tanh \frac{2n+1\pi\alpha}{2\beta}}{2n+1)^2\pi^2 - 16\beta^2} \dots \dots \dots (36),
\end{aligned}$$

whence I find—

TABLE of Stresses.

	$\beta = \pi/2.$	$\beta = 3\pi/4.$	$\beta = \pi.$	
$\alpha = \pi/6$	— 0.67631	— 0.85397	$-\infty$	} $S_A/\mu\tau c$
$\alpha = \pi/2$	— 2.0716	— 3.6144	$-\infty$	
$\alpha = \pi/6$	0.40265	0.42625	...	} $S_B/\mu\tau c$
$\alpha = \pi/2$	1.7276	2.0509	...	
$\alpha = \pi/6$	0	0.85106	...	} $S_C/\mu\tau c$
$\alpha = \pi/2$	0	2.2794	...	

We see that the greatest of the three stresses occurs at A, i.e., at the vertex of the hyperbola, and it is probable that A is the true fail-point.

The following are the values of S_A/S_0 , S_0 having the same meaning as in § 12:—

TABLE of S_A/S_0 .

	$\beta = \pi/2.$	$\beta = 3\pi/4.$	$\beta = \pi.$
$\alpha = \pi/6$	1.2101	1.1496	∞
$\alpha = \pi/2$	1.2192	1.6888	∞

The values of the "efficiency" are easily obtained.

TABLE of E.

	$\beta = \pi, 2.$	$\beta = 3\pi, 4.$	$\beta = \pi.$
$\alpha = \pi/6$	·7361	·7171	0
$\alpha = \pi/2$	·6485	·4728	0

The above results do not need any detailed discussion. We see that in all cases the maximum stress is greater than the maximum stress for the circular section. Also the efficiency is always less than unity. If we compare these values of the efficiency with those in § 19, we see that, on the whole, the rule holds that the more compact the section the higher its efficiency. On the other hand, by indenting a section we render it less efficient.

§ 24. *Conclusion and Summary.*

Looking back upon the results of the paper, we see that the study of these special forms of cross-section sheds new light upon several little-explored parts of the theory of elasticity.

It confirms to a great extent DE SAINT-VENANT'S investigations concerning the behaviour under torsion of a rail, or of shafts of similar section.

Owing to the great generality of the forms treated, it enables us to correlate the results previously obtained for sections of various shapes, especially with regard to the maximum stress. It shows us what type of cross-section will give us four fail-points not at the points of the contour closest to the centre; within what limits we may expect to find this exception to the ordinary rule; and in what manner this case passes into others.

Again, with regard to the effect of keyways upon the torsional rigidity, the results of the paper tell us that, without risk of sensible error, we may in practice, in order to get the joint effect of two indefinitely thin keyways or slits, add the known effects of each keyway, taken separately.

Further, these results bring the theory of elasticity into better accordance with observed facts, by showing that the effects of keyways of moderate depth are comparatively much smaller than would have been expected from the results for the circle.

XI. BAKERIAN LECTURE.—*The Crystalline Structure of Metals.*

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Received and Read May 18—Revised June 30, 1899.

[PLATES 15-28.]

THE microscopic study of metals was initiated by SORBY,* and has been pursued by ARNOLD, ANDREWS, BEHRENS, CHARPY, CHERNOFF, HOWE, MARTENS, OSMOND, ROBERTS-AUSTEN, SAUVEUR, STEAD, WEDDING, WERTH and others.† The work of these authors has demonstrated the value of the microscope in metallurgy, not only as an aid to analysis, but as a means of observing structure. The structure of pure metals, of metals containing small quantities of foreign matter, and of alloys, has been made the subject of microscopic examination, and important conclusions have been reached. The work to be described in this paper proceeds on the same general lines. A large part of it deals with a branch of the subject which has not hitherto received much notice, namely, the effects of strain. The writers believe that they have established the fact that the structure of metals is crystalline even under conditions which might be supposed to destroy crystalline structure. They have found that the plastic yielding of metals when severely strained occurs in such a manner that the crystalline structure is preserved. The observations to be described show how crystalline aggregates exhibit plasticity, and how, after straining, a metal continues to be a crystalline aggregate. The distinction which is often drawn between crystalline and non-crystalline states in metals appears to be unfounded.

Except for a few simple innovations, the methods of experiment used in this research, especially as regards the preparation of specimens, do not differ materially from those of earlier workers. The specimens were first polished on commercial emery-paper which had been previously rubbed on a piece of hard steel in order to remove the coarser particles. They were finished on a rapidly revolving disc coated with fine wash-leather and charged with a thin paste of rouge and water. For most purposes

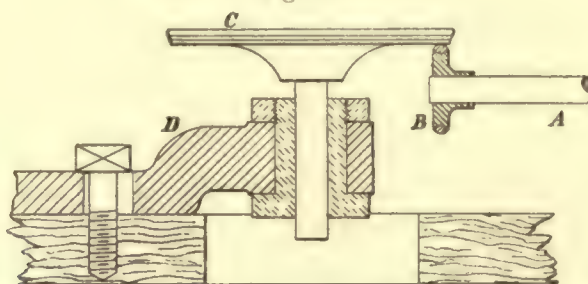
* 'Roy. Soc. Proc.,' vol. 13, p. 333.

† For the bibliography see Sir W. ROBERTS-AUSTEN'S book on 'Metallurgy' (Edition of 1895); also a paper by Mr. J. E. STEAD on the "Crystalline Structure of Iron and Steel," 'Journal of the Iron and Steel Institute,' 1898.

the finest jeweller's rouge is suitable, but in special cases we resorted to the use of peroxide of iron obtained by precipitation from a solution of pure ferric chloride.

The polishing machine is shown in diagram-section in fig. 1. *A* is the spindle of an electro-motor carrying a small driving disc *B*, fitted with a rubber ring to increase the driving friction. The polishing disc *C* is horizontal and has a vertical axis running in a bearing in the casting *D*. The under side of the polishing disc bears upon the driving wheel *B* and takes motion from it. When it is desired to stop temporarily the polishing disc is raised out of contact with the driving wheel. The

Fig. 1.



casting *D* is held to the base-board by a bolt passing through a slot which allows the disc to be brought nearer to the motor, so that it may bear upon the driving wheel at any desired distance from its axis, thus giving a means of varying the speed. More usually, however, the speed was varied by regulating the current in the motor.

With metals which are very liable to tarnish, wet polishing has to be avoided; in some cases dry rouge, and in others rouge moistened with a little paraffin, may be used—the latter we found particularly useful in polishing copper. But in some metals, especially the more fusible ones, such as lead, zinc, and tin, it is difficult to obtain a satisfactory surface by any method of polishing. In most of these cases, however, a method of obtaining a good surface entirely without polishing becomes available. This consists in pouring the molten metal on a smooth body, such as glass or polished steel, in contact with which it is allowed to solidify. We have, as a rule, used glass for this purpose, and in spite of frequent failures, due to fracture of the glass or to less obvious causes, we find that it is generally practicable to get a good specimen in this way with much less trouble than is required to produce a specimen of iron or steel by the ordinary process of polishing. This method of “glass casting” cannot well be applied to metals which oxidize at temperatures below their melting points, and for metals which have a very high melting point a smooth body other than glass must be used. The metals most readily treated by casting against a smooth surface are gold, bismuth, cadmium, lead, tin, zinc, and fusible alloys.

In the examination of lead another method of obtaining a good surface, without either melting or polishing, was also used. A face of the specimen was freshly cut to remove the tarnish, and was then pressed against a smooth surface of plate-glass. Whenever a sufficient pressure could be reached without breaking the glass a very

beautiful surface was obtained. In some cases polished steel was used as the smooth object against which the metal was pressed.

The polished surfaces were, in general, slightly etched before microscopic examination, in most instances by dilute nitric acid. Frequently, however, no etching was resorted to, especially in observations dealing with the effects of strain. It has been pointed out by CHARPY that straining, by the relative displacement which it brings about among the crystalline grains, serves to reveal the structure. Our observations confirm this, and in some cases we found that a better investigation of the effects of strain could be made when the surface was not etched.

Most of the microscopic observations were made with ZEISS' apochromatic lenses, a 2-millim. homogeneous immersion lens of 1.40 aperture being employed for high power work, with compensating eye-pieces magnifying from 4 to 18 times, giving in direct vision a total magnification up to 3000 diameters. "Vertical" illumination was generally used, the objective serving as condenser, but in some cases the specimens were examined under oblique light. Photographic records of the most interesting features were obtained, some of which are reproduced in this paper. The source of light was an arc lamp, the beam from which was condensed on the illuminator through a "Gifford" screen which allowed only a very limited portion of the spectrum to pass. Most of the high power photographs were taken with a magnification of 1000 diameters; in a few instances it was 4000 diameters or more.

It is well known that when the polished surface of a metal, such as gold or iron, is lightly etched, and is then examined by means of normally reflected ("vertical") light, the surface appears divided up into a number of areas separated by more or less polygonal boundaries. These areas are the sections of the crystalline grains which constitute the mass of the metal; the boundaries between them have been made evident by the differential action of the acid which has produced differences of level by attacking one grain more energetically than its neighbour. Fig. 2 (Plate 15) illustrates this appearance in ordinary iron. There the black patches are due to the presence of slag, and the black lines forming the boundaries are due to differences of level between the grains. Each of the short sloping surfaces which connects one grain with another appears black because it does not reflect the normally incident light back into the tube.

It is also well known that a further differential action of the acid is to reveal a difference of texture between the grains. This is visible in fig. 2, but is much more pronounced when the surface is examined under oblique light. When the light is uni-directional or nearly so, the various grains differ very much in brightness and colour—some are almost black, while others shine out brightly; if, however, the incidence of the light or the orientation of the specimen be changed, other grains shine out strongly, while those previously bright become dark. This effect was first observed in gold by ARNOLD ('Engineering,' February 7, 1896), who accounted for it by considering that each crystalline grain is built up of a very large number of what

he (following ANDREWS) calls secondary crystals, which have different orientations in different grains. Substantially the same view is expressed in other terms by OSMOND and ROBERTS-AUSTEN ('Phil. Trans.,' A, vol. 187, pp. 424-5), who speak of little crystals, "the general orientation of which remains constant in the area of each grain." Many beautiful illustrations of the same effect in iron have been given by STEAD, along with a clear discussion of the cause to which this appearance is to be ascribed ('Journal of the Iron and Steel Institute,' 1898). A striking instance is shown in his photographs of steel containing about $4\frac{1}{2}$ per cent. of silicon. The fractured ingot of this material exhibits large crystals, and by deeply etching a polished surface he has obtained a fine development of the regularly oriented elements of which the crystalline grains are built up, on a scale so large as to be clear with little or no magnification.

These observations have made it plain that each of the grains which appear on the polished and etched surface of a metal is simply a crystal, the growth of which has been arrested by its meeting with neighbouring grains. The irregular boundaries of the grains are determined by these meetings. We may imagine the grains to grow from as many centres or nuclei as there are grains. Each grain is built up of similarly oriented parts, but the orientation changes from grain to grain. Etching a polished surface develops a multitude of facets which have the same orientation over the surface of any one grain, but different orientations in different grains. Seen under oblique illumination these facets show themselves to be similarly oriented in each grain by the uniform manner in which the grain reflects light, and by the disappearance of brightness over the whole surface of the grain when the incidence of the light is changed. The mass of the grain consists of similarly oriented elements; as to the size of the elements no assumption need be made. The facets which are developed by etching do not, in general, appear of constant size; it is to the constancy of their orientation that the effect is due.

A striking illustration of how a metal crystallises by the simultaneous building up of groups of elements from a number of centres, the elements in each group being similarly oriented, while the orientation varies from group to group, may be seen in a cake of solidifying bismuth from which the still molten metal has been poured away. The operation then goes on upon a scale so large that no magnification is required to make it apparent. Fig. 3 is a photograph of a specimen of bismuth in the Cambridge University Museum of Mineralogy, for the loan of which the authors are indebted to Professor LEWIS and Mr. A. HUTCHINSON. The scale of the photograph is only about two-fifths natural size, but it shows well how the cake is made up of crystalline grains, each composed of elements with a definite orientation, the boundaries between the grains being due to the casual meeting of the several groups in the process of growth.

The references given above will show that there is nothing novel in this view of the structure of metals. Several of the authors' observations may, however, be

mentioned as affording additional evidence that the structure of metals in general consists of crystalline grains built up in the manner which has been described. One class of evidence has been obtained by an examination of specimens of iron which had been deeply etched under very high magnification, *i.e.*, 2000 to 3000 diameters. Under favourable circumstances it is possible to resolve the minute structure to which the peculiar reflection of oblique light is due. The face of each grain is then seen to be covered with minute projections resembling scales, more or less square or oblong in shape and similar and similarly oriented over the entire face of one grain. Fig. 4 is a photograph of this appearance as seen in nearly pure wrought iron: it may be compared (as Mr. STEAD compares a like appearance occurring on a large scale in silicon steel) to the arrangement of slates on the roof of a house. In other cases the action of the acid is different: the general surface of a grain cannot be resolved under the highest powers, but here and there the acid has etched out minute pits showing a distinct geometric form. All these pits found over the face of one grain are similar and similarly situated figures, but the shape and orientation of the pits changes as soon as a boundary is crossed. This is shown in a very striking way where a comparatively large pit crosses the boundary so that a portion appears on each side. Each portion preserves its proper shape and orientation, and there is consequently a marked angle in the sides of the pit where the sides cross the boundary. The shape of all these pits in iron is consistent with the assumption that they are plane sections of cubes or octahedra.

Fig. 5 (Plate 16) is a photograph of such etched pits in Swedish iron.

A good development of geometrically etched pits is not very readily obtained: in some specimens of iron they occur with much greater readiness than in others, and this occurrence is to some extent an accident of etching. Possibly the presence of a minute quantity of impurity in the iron is an essential factor, but we have no evidence on the subject. Geometrical etched pits are a well known phenomenon in non-metallic mineral crystals. BAUMHAUER* finds that they have a definite relation to the crystallographic nature of the crystal upon which they occur—but the facets developed by etching often lie in planes which are not parallel to the natural faces of the crystal. He finds that these etched pits, though generally truly geometrical, frequently show curved or irregular outlines which he attributes to local concentration of the acid. We find that curved or irregular outlines often occur in the larger etched pits in iron, and in view of BAUMHAUER's observations it is clear that they cannot be taken to affect the evidence for the strictly crystalline nature of the metal, since similar appearances are to be found in bodies that are characteristically crystalline.

When metals are cast against glass or other smooth bodies, to get a surface fit for microscopic examination, evidences of crystalline structure appear apart from any-

* BAUMHAUER, 'Resultate der Aetzmethode in der Krystallographischen Forschung.' WILHELM ENGELMANN, Leipzig, 1894.

thing that is shown by etching. The cast surface generally shows clearly, without any etching, the boundaries between the crystalline grains. Good examples of this are found in cadmium, lead, tin, and zinc. In some instances the boundaries between the grains are emphasised in a remarkable way by the accumulation there of air or of gas given off by the metal during solidification. The boundaries then appear as more or less deep and wide channels. As the growth of the crystalline grains proceeds most of the air or gas which has been entrapped between the glass and the metal, and most of the gas given out from solution in the metal itself, tends to accumulate at the boundaries, which are the last parts of the surface to undergo solidification. A network of channels consequently appears on the surface next the glass; in general these channels coincide with boundaries, but occasionally a channel forms a *cul-de-sac* or terminates in a large cavity which is obviously a bubble or blow-hole. Fig. 6 shows the appearance of a surface of cadmium cast against glass under conditions of temperature favourable to the formation of these channels. By etching or straining the specimen it is easy to prove that each channel (except when it is a *cul-de-sac* formed by excess of gas) coincides in general with a real boundary between the crystalline grains. The true boundary is merely the trace of a surface on the plane of casting, but it may be broadened out in this way, by the presence of gas, into a shallow channel of considerable width. It is only in certain conditions of temperature, on the part of the metal and of the body against which it is cast, that any marked development of such channels is obtained. Under most conditions, however, it is easy to distinguish the intergranular boundaries in the cast surface, either by the presence of some gas there or by slight differences of level between one grain and the next.

Occasionally the faces of some of the grains in the surface cast against glass are covered with a number of very minute pits, whose true character appears only under a magnification of about 1000 diameters. They are then seen to be pits of definite geometrical form both as to outline on the surface and as to inner facets. Figs. 7, 8, and 9 are photographs of these pits in glass-cast cadmium. It will be seen that they are systems of geometrical figures which remain similar and similarly situated over the entire surface of a single grain, but change in character from one grain to the next. These pits appear to be excessively small bubbles or blow-holes which have taken a geometrical shape, forming, in fact, negative crystals. During the crystallisation the crystalline elements have built themselves around the gas bubbles in regular orientation, finally leaving the pits as we see them. In support of this view the appearance seen on fig. 8 may be cited; the pits are seen to be surrounded by a halo or circular patch of bright surface—due apparently to the absorption by these larger geometrical bubbles of the numerous tiny bubbles that dot the surface elsewhere.

The photographs show these “air-pits” in cadmium cast against glass under a magnification in most cases of 1000 diameters, and in one case (fig. 9) of 4200

diameters. The characteristic of the pits is that they are similar and similarly oriented over any one grain, but on passing from one grain to another, across a boundary, the orientation of the pit is found to have changed. Good examples of this are seen in fig. 7, where the boundaries are widened out into channels through the presence there of air or gas in the manner described above. This characteristic of the air-pits is, of course, in complete conformity with the view already stated of the crystalline structure of metals. Additional photographs of air-pits in cadmium are shown in another connection in figs. 26, 27, and 28 (Plates 22 and 23).

Examination of the air-pits in cadmium shows that the forms may be accounted for as sections of hexagonal prisms. It may be concluded that each crystalline element of which the grains of cadmium are built up is a hexagonal prism with plane base.*

These air-pits are not very readily developed, and the precise conditions which determine their appearance are not easily specified. Many specimens of the metal may be cast without obtaining them. That they are not, however, peculiar to cadmium is certain, for we have found them also in tin and in zinc. Fig. 10 shows them in a glass-cast surface of tin.

The same photograph illustrates another interesting feature. The surface of the tin is seen to be covered with a multitude of small dark crystals irregularly disposed. These are evidently inclusions of some foreign matter, which we conjecture to have been sulphide, because it was observed that they appeared in large numbers after the metal had, during melting, been directly exposed to a gas flame. The foreign crystals have no definite orientation, and are quite independent of the orientation of the metal within the grains in which they are embedded. The crystallisation of the metal has proceeded around them without check or disturbance, just as in iron containing slag the growth of each crystalline grain ignores the presence of that impurity. It is well known that a slag band is often seen running right through a crystalline grain without affecting the uniformity of orientation of the elements of which the grain is built up.

Although it must be admitted that a really good development of geometrical bubbles such as those shown in the photographs is exceptional and cannot as yet be reproduced at will, the authors have observed that nearly all bubbles or blow-holes found on surfaces prepared in this way show a distinct tendency to geometrical shapes. A truly round bubble is rarely or never found, and even the larger bubbles often show a multitude of distinct facets reflecting light at different angles.

The occurrence of such geometrical pits in surfaces of metals that have never been polished or etched may be taken as very strong evidence in support of the view that

* It may be added in this connection that BEHRENS remarks on the frequency of six-sided forms in the polygonal boundaries of the crystalline grains of cadmium. The form of boundary is, however, of little service in determining the character of the crystallisations within the grain. (See his work '*Das Microscopische Gefüge der Metalle und Legierungen*,' Leipzig, 1894.)

the crystalline grains of metals are built up of crystalline elements which are similarly oriented throughout the mass of each grain.

The experiments now to be described were intended to throw light on the nature of plastic strain in metals, and the results obtained are interpreted by the aid of the theory of the crystalline structure of metals, of which an outline has been stated at the beginning of this paper. Their complete agreement with that theory affords further confirmation of its truth.

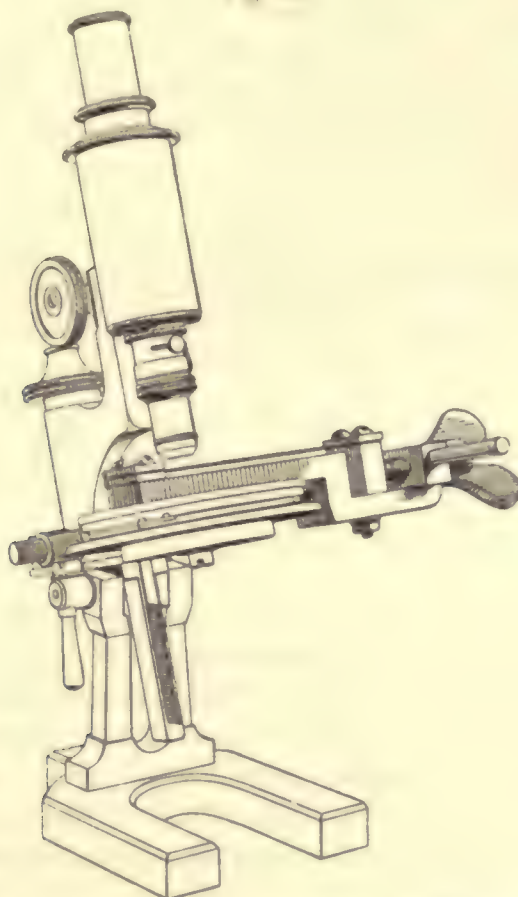
It has long been known that when a specimen of iron or steel with a bright smooth surface is strained sufficiently to give it permanent set the smoothness of the surface is destroyed. A microscopic examination of the surface shows, as CHARPY has pointed out, that the crystalline grains become visibly differentiated from one another by straining, and the effect is in this respect not unlike that which etching would have produced. There is, however, a further effect of straining, which will be described immediately.

It is also well known that when a piece of severely-strained metal is polished and etched, as for instance a bar which has had its section reduced by hammering or rolling in the cold state, the crystalline grains are found to have changed their form. They are lengthened in the direction in which the piece was extended and shortened in the direction in which the section has contracted. Accordingly, a severely-strained piece is readily recognised on polishing and etching it, on account of the shape of its crystalline grains. In the strained specimen these are found to have a direction of predominating length according to the direction of strain, while in the unstrained specimen there is no direction of predominating length. Further, it is well known that in a strained specimen elongated grains are not found after the strained state has been relieved by annealing. The effect of rolling or hammering is often spoken of as a conversion of the metal from a crystalline to a "fibrous" state. In the present writers' view this language is misleading, and the physical conception underlying it is a mistaken one.

In the first experiments on the effects of strain we aimed at keeping a particular place on the polished and etched surface of the specimen under continuous observation while the specimen was being strained. This was accomplished by constructing a small straining machine which could be attached to the stage of the microscope, and by which strips of sheet metal could be gradually extended until they broke. Fig. 11 shows the arrangement which was used. The stress was applied by a screw which could be turned by hand while the specimen was under observation, and any displacement of the particular grains on which the microscope was focussed could be made good by means of the traversing screws in the mechanical stage. With this apparatus it was easy to keep the same group of crystalline grains under observation from the first application of stress until the specimen was broken, and to obtain photographs of the same group at any number of stages during the strain. The first specimens observed in this way were strips of sheet iron, of the nearly pure kind supplied for

use in electrical transformers. The following account of what we have observed may be read as applying not only to iron but to other metals. Within the limit of elasticity no effects of strain are detected, but when the yield point is reached a remarkable change is seen on the surface of the crystalline grains. As soon as plastic deformation begins the faces of the grains show fine black lines, and as the strain increases these lines increase in number; they are more or less straight and parallel in each grain, but are differently directed in different grains. The first lines to appear are those approximately transverse to the pull, but as the strain increases systems of

Fig. 11.



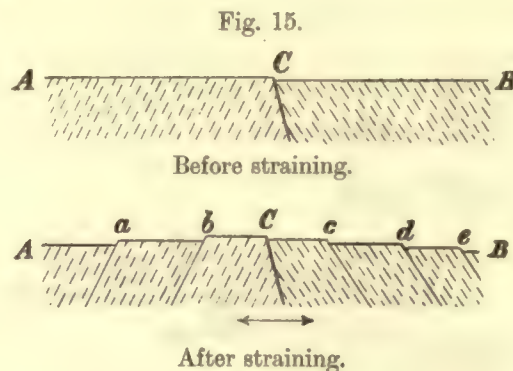
inclined lines appear on other grains. With further straining some of the grains begin to show more than one system of such lines, and eventually two, three, and even four systems of intersecting lines on a single grain may be seen.

A characteristic example of these lines as exhibited by iron is shown in fig. 12, which is a photograph of a piece of Swedish iron strained by pull. Figs. 13 and 14 are two views of the same group of crystalline grains in another piece of Swedish iron, fig. 13 being taken before straining, and fig. 14 after a considerable amount of straining. When the piece is much strained the surface becomes so rough as to make it difficult to secure a satisfactory photograph.

The appearance of the grains after straining so closely resembles that of a crevassed glacier that the black lines might be taken for cracks. But from the outset it was clear that they could not be actual fissures. A piece of strained iron, when it has been allowed to rest for a time, or has been heated to 100°C .,* recovers its original elasticity and more than its original strength, yet the dark lines do not disappear under such treatment. Further, if a specimen showing these lines be re-polished the lines disappear, and even light etching does not reproduce lines of the same nature.

The real character of the lines is apparent when the crystalline constitution of each grain is considered. They are not cracks but steps in the surface. These steps are due to slips along the cleavage or gliding planes of the crystals.†

The diagram, fig. 15, is intended to represent a section through the upper part of two contiguous surface grains, having cleavage or gliding places as indicated by the dotted lines, A B being a portion of the polished surface, C being the junction between the two grains.



When the metal is strained beyond its elastic limit, as say by a pull in the direction of the arrows, yielding takes place by finite amounts of slips at a limited number of places, in the manner shown at *a, b, c, d, e*. This exposes short portions of inclined cleavage or gliding surfaces, and when viewed in the microscope under normally incident light these surfaces appear black because they return no light to the microscope. They consequently show as dark lines or narrow bands extending over the polished surface in directions which depend on the intersection of the polished surface with the surfaces of slip.

The correctness of this view is demonstrated when these bands are examined under oblique light. When the light is incident at only a small angle to the polished surface, that surface appears for the most part dark; but here and there a system of the parallel bands shines out brilliantly in consequence of the short cleavage surfaces which constitute the bands having the proper inclination for reflecting light into the microscope. The groups of bright bands which are seen under oblique light are

* See J. MUIR "On the Recovery of Iron from Overstrain," 'Phil. Trans.,' A, 1899.

† See 'Roy. Soc. Proc.,' March 16, 1899 (vol. 65, p. 85), where the authors have published a preliminary account of some of these observations.

readily observed under the microscope to be exactly coincident with the black bands seen under vertical illumination. Figs. 16 and 17 are photographs of the same strained crystalline grains of iron under vertical light and under oblique light.

Rotation of the stage upon which the strained specimen is fixed makes the bands on one or another of the grains flash out successively with kaleidoscopic effect. When the specimen is rotated through 180° from the position in which the lines show brightly on one particular grain, the lines on that grain do not shine out again, though they may be visible as black lines on a very faintly luminous background; this is important as proving that the lines are not due to either furrows or ridges, but to steps in the surface. In this respect there is a striking contrast between the slip-bands and any accidental furrows or scratches which may have been left on the specimen through imperfect polishing.

Incidentally, fig. 17 illustrates the fact that oblique light picks out the boundaries of the crystalline grains, showing that these boundaries are marked by inclined surfaces connecting grains whose faces are at different levels. This is observed also in the etched surface of the metal before straining. The boundaries, which appear dark under vertical light, are bright on one side of each crystalline grain when the light falls with grazing incidence from one side; but the sloping surfaces which mark the boundaries between the grains have not the sharply-defined inclination of the slip-surfaces. The lines due to slip-bands on one or more grains will shine out brightly when the light has a particular angle of incidence, and will vanish when the incidence is slightly changed. The boundaries are generally not so bright, but remain visible under a considerable range of incidence.

Figs. 18, 19, and 20 present a striking example of the kaleidoscopic effect under oblique light just referred to. Here the metal is lead, the surface has been obtained by allowing molten lead to solidify on a smooth glass plate, and the metal has been strained by bending. The figures show the appearance under vertical light and also under two different incidences of oblique light. Figs. 21 and 22 show another example of strained lead under vertical and oblique light.

In their preliminary notice* of some of the present results (communicated to the Royal Society on March 16, 1899) the authors have applied the name "slip-bands" to the lines developed on metallic surfaces by plastic strain, and in what follows they will be referred to under that name.†

So far as the writers' observations go it appears that slip-bands occur in all metals

* "Experiments in Micro-metallurgy: Effects of Strain," 'Proc. Roy. Soc.,' vol. 65, p. 85. Since writing that paper the authors' attention has been directed to the following remark by Mr. STEAD:—"It would appear that there is a tendency for iron to etch out into thin plates, and when such etched specimens are distorted or pulled out for these etched plates to slide over one another" ("On Brittleness Produced in Soft Steel by Annealing," 'Journal of the Iron and Steel Institute,' 1898). It will, however, be shown presently that the development of slip-bands is independent of any previous etching.

† "Experiments in Micro-metallurgy: Effects of Strain," EWING and ROSENHAIN, 'Roy. Soc. Proc.,' 1899, vol. 65, p. 85.

as soon as plastic deformation takes place. They have been observed in specimens of platinum, gold, silver, copper, lead, zinc, tin, cadmium, bismuth, aluminium, iron, and nickel, as well as in steel, brass, bronze, and other alloys. In the case of iron it was proved definitely that under tensile stress the bands appear as soon as the yield point is passed. For this experiment a flat was polished on the side of a test-piece, which was strained in a 50-ton testing-machine, and the surface was kept under observation, during the application of the stress, by means of a microscope hung from the bar itself.

Slip-bands are developed by all kinds of strain involving permanent deformation of the piece. A microscopic inspection of the surface after straining does not enable us to detect whether the deformation has been caused by tension, compression, bending, or torsion, but the appearance depends very much on the amount of strain that has taken place. The more severely the specimen has been strained the greater is the number of slip-bands developed. After slight straining there is generally only one system of bands to be seen on each crystalline grain, but as many as four such systems intersecting one another may come into view after severe straining. Fig. 23 (Plate 21) is a photograph of strained lead, showing four systems of slip-bands.

The general appearance of the slip-bands is different in different metals. In lead they are particularly straight, even under extreme magnification, as is illustrated in fig. 24. In silver there is a tendency to more wavy outlines, as appears in fig. 25, Plate 22, but in gold the lines are as straight as those in lead. In iron the lines tend, as a rule, to be rather wavy, and to fork and branch. Examples of slips in this metal have already been given in figs. 12, 14, and 16; others have been given in the preliminary notice referred to above.*

In gold, lead, and other metals showing straight slip-bands it is easy to distinguish well-marked steps where intersecting systems cross. Fig. 24 is a characteristic example.

In several specimens of lead, prepared by casting against glass, a peculiarity was noticed which forms an apparent exception to the statement made above that slip-bands which shine out under oblique light at one particular incidence do not reappear when the incidence is changed (*i.e.*, the specimen rotated) by 180° . The specimens in question were examined under oblique light with an objective of 16 millims. focus, giving a magnification of 100 diameters. On rotating the stage carrying the specimen the slip-bands on one crystalline grain were found to shine out strongly in two positions, very nearly 180° apart. Under this low magnification it seemed that identical bands were visible in both positions; but on applying a power of 2000 diameters with a combination of "vertical" light and an oblique beam of grazing incidence from an arc lamp it was seen that there were really two systems of parallel slip-bands on the same crystalline grain, and that only one of them was picked out by the oblique light. In the other system of slip-bands the slope of the cleavage surfaces exposed by the slips was inclined away from the source of light, and consequently remained dark. The

* 'Roy. Soc. Proc.', vol. 65, Plates 1-5.

explanation, then, is that in this grain the crystalline elements are oriented in such a way that the intersection of two sets of cleavage or gliding planes is parallel to the surface, and consequently their traces on the surface are parallel to one another. This seems to be an accidental occurrence, possibly favoured by the condition under which the specimen crystallised, namely in contact with cold glass. In many other instances a more or less close approximation to such parallelism has been observed, resulting in systems of slip-bands intersecting at a very small angle; in that case the two positions where slip-bands appear under oblique light are nearly, but not exactly, 180° apart. Seen under vertical light, with low magnification, such intersecting systems produce the appearance which is exemplified in the central grain in fig. 18, Plate 19.

The relation of slip-bands to the geometrical air-pits in cadmium is illustrated by the photographs, figs. 26, 27, and 28. In these examples the metal was cast against glass in such a way as to produce air-pits, and was then strained sufficiently to develop slip-bands. It appears that the slip-bands are always parallel to one side of the geometrical pits—the two phenomena thus confirming the views which have been advanced above as to the crystalline structure of the metal. Figs. 29 and 30 show the relation of slip-bands to geometrical etched pits in iron. It will be observed that the slips are not generally parallel to a side of the etched figures, but in specimens that have been more severely strained than those here illustrated, one set of slip-bands in each grain is generally found to be parallel to one side of the etched pits, while the other systems intersect these sides diagonally. The observations point to the conclusion that in iron slipping occurs most readily along the octahedral planes, although slips parallel to the sides of the cubical crystals are also found.

The development of slip-bands in strained metal throws what appears to us to be a new light on the character of plastic strain. Plasticity is due to the occurrence of these slips. When metals are strained beyond their limit of elasticity the deformation occurs through sliding over one another of the elementary portions of which each crystalline grain is built up.

The sliding which gives rise to slip-bands is of finite amount, and occurs at a limited number of places. "Flow" or plastic strain in metals is not a homogeneous shear such as occurs in the flow of a viscous fluid, but is the result of a limited number of separate slips.

The conception that metals adapt themselves to the new shapes imposed upon them when they undergo plastic deformation by means of slips along cleavage or gliding planes within each crystalline grain, leads naturally to the supposition that the crystalline elements themselves undergo no deformation in this process. The portions of the metal between one surface of slip and the next may remain undeformed, except elastically, under all stresses. The effect of a stress sufficient to produce plastic strain is analogous to that of a tractive force overcoming the static friction between two surfaces.

If we assume that plastic strain takes place solely by these slips, it follows that the ultimate crystalline elements should always remain parallel to themselves. The orientation of the elements would remain uniform throughout the mass of one grain, however much the outline of that grain were distorted by slips occurring within it. In other words, the crystalline structure of a metal should survive even the severest strain.

This conclusion is borne out by the fact that in metals which have been much strained we find evidence of crystalline structure similar to that which is found in unstrained metal.

Taking this evidence in the same order as before, we would refer first to the appearance which is presented in severely strained metal, by a polished and etched section when seen under oblique light. We have examined a bar of fine Swedish iron (kindly supplied by Messrs. EDGAR ALLEN and Co.), which had been for the purpose of these experiments rolled in the cold state from a diameter of three-quarters of an inch to a diameter of half an inch, and had not been subsequently heated. A longitudinal section of this cold-rolled bar showed a great lengthening of the crystalline grains in the direction of rolling, and even in the transverse section it was obvious that the grains had been much distorted, though there was no direction of predominant length. Under oblique light both sections (longitudinal and transverse) exhibit the effect described above for unstrained metal—the grains are distinguished from one another by differences of brightness, which vary when the incidence of the light is altered, and this brightness is uniform over the entire surface of each grain. As in the case of unstrained metal, we regard this as evidence of the uniform orientation of the crystalline elements throughout each grain. Fig. 31, Plate 23, is a photograph under oblique light of a specimen of this bar cut transversely, and polished and etched. It illustrates the uniform brightness of each grain, due to uniform orientation. Similar characteristics have been observed in many other specimens of severely strained metal.

Another line of evidence in proof of the persistence of crystalline structure after severe straining is afforded when a polished specimen of, say, cold-rolled iron is subjected to a slight further strain. The slip-bands appear as they would have done had the specimen never been strained before. The general features are much the same as in annealed metal, but they show on the whole a greater tendency towards sudden steps and branches. This difference in the character of the slips may be connected with the well-known fact that such strained material is considerably harder, in the sense of having a higher yield-point and less capability of plastic deformation than it shows in the virgin or annealed state, and also with our own observation that the slip-bands are much more straight and regular in very plastic metals, such as lead, gold, and copper, than in harder metals like iron and nickel. The mere fact that finite slips occur at intervals throughout the grain implies that it is easier for sliding to take place over certain surfaces than it is over others. The surface on which

uniform slip occurs is not necessarily plane; it may be the trace of a straight line moving parallel to itself; a line which is in the direction of slip and always lies parallel to one of the cleavage planes. For convenience in argument we may for the moment assume that the surfaces of easiest sliding are determined by some accident, such as the presence there of minute layers of some impurity, such as occluded gas. If, as the straightness of the slip-bands seems to indicate, these surfaces are true planes in plastic metals like lead or gold (so far as each individual grain is concerned), sliding might take place in two directions on each of these planes. But when sliding has once taken place, the intersecting layers of impurity would no longer be distributed over planes, and further sliding on transverse planes would necessitate the starting of fresh slips in surfaces that had no special tendency to facilitate sliding. This suggests how such a metal may be hardened by previous straining; and how, also, the slip-bands formed on re-straining a piece of metal hardened in this way would be less straight and more liable to sudden steps and branches than those that are found in the virgin material; the slips would, as far as possible, follow the old surfaces of easy sliding, but these would now be stepped instead of plane as before.

A striking proof of the persistence of crystalline structure in metals which have been submitted to severe distortion is found in the existence of geometrical etched pits. These are readily developed in sections cut from cold-rolled iron, and they differ in no way from the etched pits developed in the virgin material; like these, they appear as similar and similarly oriented geometrical figures over the face of each grain. Fig. 32 is the photograph of a group of crystalline grains in the specimen of cold-rolled Swedish iron referred to above (cold-rolled from three-quarters of an inch to half an inch diameter). Among them is a large grain (showing light in the figure) with an outline so unlike those found in unstrained metal that its form is evidently due to violent distortion in the process of rolling. The face of this grain is covered with minute etched pits, and an examination of these under high powers shows that they have preserved their similarity of shape and orientation in spite of the violent distortion which the grain, as a whole, has undergone. Fig. 33 is a photograph under 800 diameters of a portion of the large grain in question, which appears near the middle of fig. 32.

From the various lines of evidence here indicated we conclude that the characteristic crystalline structure of metals is not destroyed by strain, no matter how severe, and that plastic deformation occurs by means of slips along the cleavage or gliding planes of the crystalline grains, the crystalline elements which build up each grain remaining unaltered both as to shape and orientation. This statement, however, is subject to the following qualification. We have found in certain metals, notably copper, gold, silver, lead, cadmium, tin, zinc, and nickel, that twin crystals are liable to be developed by straining. Hence in such cases it is not exact to say that straining produces no change in the orientation of the crystalline elements, for twinning implies a rotation of one group of elements with respect to the rest through a

definite angle. The twinning which we have found in many strained metals corresponds to the twinning observed in calcite by BAUMHAUER and REUSCH, and subsequently produced in isolated crystals of antimony and bismuth by MUGGE.*

BAUMHAUER found that by forcing a knife blade into a crystal of calcite at the proper angle a portion of the crystal could be made to swing over into the twinned position. This implies a corresponding change of orientation in the crystalline elements. The experiment may be said to afford an example of plasticity in a crystal, but it is not entirely analogous to the plasticity by pure sliding which is found in iron and in most other metallic crystals. In the process of twinning by strain there is both slip and rotation of the elements.

The existence of twin crystals in certain metals became apparent when systems of slip-bands were found like those shown in figs. 34, 35, and 36. These are photographs from specimens of copper. They show that certain of the crystalline grains are crossed by twin lamellæ, the twin planes being defined by a sudden change in the direction of the slip-bands. Where several such twin lamellæ occur in one crystalline grain, we have a periodic structure with alternate systems of parallel slip-bands. The change of orientation in passing from one lamella to another is constant. It is clear that in these examples we have true cases of twin crystallisation. An example of twinning in gold, as seen under vertical light, is given in fig. 37, and fig. 38 is a photograph of twins in gold, seen under oblique light.

The question arose whether these twin crystals were a feature in the primitive crystallisation of the metal, or whether they were subsequently produced as a consequence of strain. They were first seen in wrought copper (namely in a piece of rolled plate), which had been raised to a bright red heat before polishing. We next examined specimens of copper, gold, silver, and lead, each in the cast state, and in none of these found any appearance of twinning. For the purposes of this examination only a slight strain was applied. The same pieces were then wrought, that is to say they were severely strained (namely, by cold hammering) and they were again examined both before and after annealing at a red heat. The result showed that the violent strain produced by working the metal had developed twins in specimens where none could be seen before, and that the twins were still found in the wrought specimens after annealing. Fig. 39 is a photograph of a "twin" in cold-hammered copper (not heated after hammering); incidentally it illustrates the persistence of crystalline structure after violent deformation. Still more striking in this respect is the appearance shown in fig. 40. The specimen in this instance was an ordinary piece of plumber's sheet lead; the surface was scraped bright with a knife, and was then squeezed against a piece of plate-glass in a vice, thus producing a beautiful surface. The specimen was then very slightly bent in the fingers to develop slip-bands, and on examination under a high power it showed the appearance reproduced in the photograph.

* See P. GROTH's 'Physikalische Krystallographie.' Voss, Leipzig.

Twinning, as revealed by slip-bands, has been observed in nickel; in this case the specimen was a virgin casting, but the twin (shown in the photograph, fig. 41) was observed only after very severe straining, and was, in all probability, produced by that straining.

In zinc, tin, and cadmium twins either occur very freely in the cast metal, or else are very readily produced by the slight strain which is applied to develop slip-bands. Surfaces of these metals, produced by casting against glass, show twin bands even under fairly low powers when the specimen is slightly bent; the twin bands then appear as shaded bands running across the crystalline grains. Very frequently the twin bands run on continuously across two or more grains, with more or less change in direction when they cross a boundary.

A specimen of cadmium showing this feature is photographed in fig. 42. This particular specimen presents another peculiarity; it was prepared by casting against glass, and in this instance the glass surface was intentionally given a considerable slope, with the result that the metal solidified in a long strip while it was running down the glass. On examining the under face of this strip two modes of crystallisation were observed. Part of the surface there showed a very small structure with no direction of greatest length. On another part there were large grains very considerably longer in the direction of the length of the strip than in a transverse direction. The photograph, fig. 42, is taken from an area showing these long grains. When the piece was strained by bending, twin lamellæ appeared in a more or less transverse direction, passing across from one elongated grain to the next with only a slight change in direction. The twin band in one grain is associated with a twin band in a neighbouring grain, the bands being continuous except for a change of direction as they pass from grain to grain.

We have observed twinning in gold, silver, copper, lead, nickel, zinc, tin, and cadmium. It does not appear to occur in iron.

The facility with which most metals undergo twinning as a consequence of strain shows that there are in general two modes by which plastic yielding takes place in an aggregate of crystals. One is by simple slips, where the movements of the crystalline elements are purely translatory, and their orientation is preserved unchanged. The other is by twinning, when rotation occurs through an angle which is the same for each molecule in the twinned group. Both modes are often found in a single specimen of metal, and even in a single crystalline grain. Thus, in gold or copper, it is very usual to find, on examining a strained specimen that one portion of a grain is covered with simple slip lines, while another portion of the same grain shows one or more lamellæ which are twinned with respect to the rest of the grain.

On surfaces prepared by casting against glass, particularly with cadmium, but also with zinc and tin, a curious feature often occurs which is closely associated with the facility these metals show in developing twins. The appearance in question is that of an apparent duplication of the inter-granular boundaries, as seen in the cadmium

casting, fig. 43. The second system of boundaries consists, like the first, in polygonal markings, and has such an obvious relation to the first that it almost appears as though the upper layer of crystalline grains were transparent, and that we were seeing their lower edges. To decide as to which of the markings on the surface constituted the true surface boundaries, two methods were available: etching with an acid and slightly straining the specimen so as to develop the slip-bands. The latter method is much the more instructive, and its results are confirmed by the etching process. When a specimen having this characteristic was strained, it was seen at once that some of the apparent boundaries were consistently ignored by the slip-bands, the others being the real junction lines of the grains. But the true nature of the pseudo-boundaries comes out on examining them under a high power. Although under low powers there is no obvious difference in definition between the genuine and pseudo-boundaries, under greater magnifications it becomes impossible to focus the pseudo-boundaries at all—they are seen to be more or less ill-defined slopes or changes of level, whereas the real boundaries are sharply defined. In general the real boundaries show some accumulation of gas bubbles along them, and they are never crossed by slip-bands. The pseudo-boundaries are found to consist in small variations of level in the surfaces of the grains in which they occur. Fig. 44 is a high-power photograph of a set of real and pseudo-boundaries showing slip-bands.

It will be noticed that on the two sides of a real boundary the slip-bands are independent of one another, whereas the slip-bands cross a pseudo-boundary with only a slight change of inclination, which is to be ascribed to the fact that the surface under examination is not a true plane. There is a slight slope on each side of the pseudo-boundary, and the lines are consequently more or less inclined to one another. Again, as we have noticed in other examples, the slope is not as a rule constant and hence the lines are slightly curved.

An explanation of this appearance of pseudo-boundaries is, we think, to be found in the strains set up by contraction on cooling. If we suppose the outer layer of crystals to cool more rapidly than the inner ones, the resulting contraction will drive the projecting edges of the lower layer into the outside grains and thus cause slight local deformation, which will project itself on the surface, probably by means of twin bands running through the grains and appearing on the surface. The effect resembles that of a Japanese "magic" mirror, in which slight inequalities of the surface, corresponding to a pattern behind, cause light reflected from the mirror to produce an image in which a ghost of the pattern may be traced.

The foregoing conclusions refer to experiments on pure or nearly pure metals. We have also examined the effects of strain on various alloys. The micro-structure of alloys has received attention at the hands of most of the workers already named, especially BEHRENS, CHARPY, GUILLEMIN, OSMOND, ROBERTS-AUSTEN, and STEAD. Our observations have been directed towards supplementing theirs, in respect particularly of the effects of strain.

The experiments on iron were extended to certain steels. In very mild steel slip-bands can be readily observed in what are generally called the "ferrite" areas, which remain white after light etching. This is shown in fig. 45. The first effect of strain is to develop the inter-granular junctions in these white areas, then more severe straining makes the slip-bands appear. In steels containing larger proportions of carbon, the scale of the granular structure of the "ferrite" diminishes and the slip-bands become correspondingly minute, requiring the highest powers of the microscope for their observation. We have not been able to observe anything of the nature of slip-bands in the dark or "pearlite" areas of steel, but the correspondence which has been recognised by OSMOND to exist between the structure of "pearlite" and that of typical eutectic alloys, taken with facts to be described below, points to the possibility that "pearlite" may also yield plastically by slipping.

Slip-bands have also been observed in various specimens of brass and bronze.

The behaviour of eutectic alloys under plastic strain is of special interest, because these bodies apparently differ so widely in structure from pure metals. Our observations have been made on the eutectics of lead-tin, copper-silver, and lead-bismuth. The micro-structure of such eutectics has been described by OSMOND.

Fig. 46 is from a specimen of lead-tin eutectic kindly prepared for us by Messrs. HEYCOCK and NEVILLE; the surface was obtained by casting against glass, and was lightly etched with a 1 per cent. solution of nitric acid. Figs. 47 and 48 illustrate the most obvious effect of strain on such structures; the surfaces have not been etched, the differentiation of the two constituents by differences of level being here entirely due to strain. It will be observed that the scale of this structure is similar to that of the slip-bands seen in pure metals, and examination of strained specimens shows that plastic yielding is associated with slips occurring between layers of the two constituents. A close examination of strained specimens has enabled us to detect slip-bands in the light-coloured constituent. By adopting the device of slow cooling, which has led to such excellent results in the hands of Messrs. HEYCOCK and NEVILLE, we have succeeded in producing specimens of eutectics in which the characteristic structure is developed upon a much larger scale. Fig. 49 exemplifies this in the eutectic of bismuth and lead, and shows slips which occur in the white constituent as a consequence of straining. This photograph illustrates a feature very characteristic of eutectic alloys; a parallel system of slip-bands extends over many patches of the white constituent, thus pointing to the fact that the crystalline elements are similarly oriented throughout considerable areas of at least one of the two constituents of the alloy. This suggests that the alloy as a whole has comparatively coarse granular structure, and the same conclusion is borne out by observing the general character of a surface under lower magnifications (such as 100 diameters), when its structure is revealed either by straining or etching. The surface is then seen to be divided into rather large more or less polygonal areas, each covered with a system of ribs radiating

from one point, giving an appearance which resembles roughly the ribs of an umbrella. Fig. 47 incidentally shows the boundary of two such areas.

In the course of experiments on the lead-bismuth eutectic, specimens were obtained showing comparatively large isolated crystallites. When the piece was strained these crystallites were found to exhibit slip-bands. Examples are given in figs. 50 and 51. These are interesting as showing the development of slip-bands in bodies which are evidently fully developed crystals, even as to external form.

A study of the micro-structure of alloys suggests a possible explanation of the peculiarities they present in regard to variation of electrical conductivity with temperature. The two constituents may behave individually as pure metals in this respect, but if their coefficients of expansion are different the closeness of the joints between them will depend on the temperature. Thus, if the more expansible metal exists as plates or separate pieces of any form within the other, the effect of heating will be to make the joints between the two conduct more readily, with the result of reducing the increase of resistance to which heating would otherwise give rise, and in extreme cases with the effect even of producing a negative temperature coefficient.

Reviewing the general results of the experiments, we consider that they establish the view that the structure of metals in general is crystalline, and remains crystalline when the form of the metal is altered by strain, plastic yielding being due to slips on cleavage or gliding planes within each individual crystalline grain, and partly (in some metals) to the production of twin crystals. In a pure metal, when straining is carried far enough to produce fracture, the crystalline grains suffer cleavage, and the cleavage surfaces thus developed give to the fracture its characteristically crystalline appearance. In impure metals fracture may occur through the parting of grains from one another at their boundaries. In both cases, however, the plastic yielding which precedes fracture takes place by slips in the manner we have described.

In conclusion we should like to express our indebtedness to Sir W. ROBERTS-AUSTEN, Mr. T. ANDREWS, and Professor ARNOLD, for giving us at the outset of our work the benefit of their large experience in preparing specimens of metals for microscopic examination. Messrs. HEYCOCK and NEVILLE and Mr. A. HUTCHINSON have assisted us materially by various suggestions, and by supplying specimens for examination. We have also to thank Mr. ANDREWS, Mr. STEAD, Mr. HADFIELD, Professor HICKS, and Messrs. EDGAR ALLEN and Co. for special specimens of iron.

The work described in this paper was carried out in the Engineering Laboratory at Cambridge.

To facilitate reference to the illustrations an index is added in which brief particulars are given of the subject of each photograph.

EXPLANATION OF FIGURES ON THE PLATES.

PLATES 15-28.

PLATE 15.

- Fig. 2. Nearly pure commercial iron (transformer plate), polished and etched. Magnified 200 diameters, vertical illumination.
- Fig. 3. Photograph of bismuth crystals, from a specimen in the Cambridge University Mineralogical Museum. $\frac{2}{3}$ ths of full size.
- Fig. 4. Facets on a crystalline grain of iron, produced by etching. These facets give rise to differences of brightness when the grains are seen under oblique illumination. Magnified 1500 diameters, vertical light.

PLATE 16.

- Fig. 5. Etched pits in Swedish iron. 1000 diameters, vertical light.
- Fig. 6. Surface of cadmium cast against glass, showing crystalline boundaries emphasized by air-channels. 100 diameters, vertical light.
- Fig. 7. Air-pits on a glass-cast surface of cadmium. 1000 diameters, vertical light. Pits are shown on three crystals, having a different shape and orientation on each.

PLATE 17.

- Fig. 8. Air-pits on a glass-cast surface of cadmium. 1000 diameters, vertical light. The pits are surrounded by halos due to the absorption of smaller bubbles by the pits.
- Fig. 9. Similar pits to those in figs. 7 and 8, but more highly magnified—4200 diameters. The photograph shows that the pits have geometrical inner faces.
- Fig. 10. Air-pits in glass-cast tin. Magnified 1000 diameters, vertical light. The irregularly oriented black patches are crystals of an impurity.
- Fig. 12. Slip-bands in Swedish iron strained by tension. 400 diameters, vertical light. The photograph shows a feature that is frequently observed, viz., a tendency in the lines to become curved near the inter-crystalline boundaries, suggesting the existence of keyed steps at the boundaries.

PLATE 18.

- Figs. 13 and 14. Two views of the same crystalline grains in iron before and after straining. Magnified 200 diameters, vertical light. Close comparison of

the two will show the amount by which the crystalline grains have been extended.

Fig. 16. Strained Swedish iron. Magnified 300 diameters, vertical light.

Fig. 17. The same field as in fig. 16, with the same magnification, but seen under oblique light. The slip-bands on a few grains only are picked out as bright bands.

PLATE 19.

Fig. 18. Slip-bands developed on a glass-cast surface of lead when strained by bending. Magnified 100 diameters, vertical light.

Fig. 19. The same field as in fig. 18, seen under oblique light.

PLATES 20 AND 21.

Fig. 20. The same field as in figs. 18 and 19, seen under oblique light after the stage carrying the specimen had been turned through about 15° .

Fig. 21. Slip-bands in lead. 100 diameters, vertical light.

Fig. 22. The same field as in fig. 21, seen under oblique light.

Fig. 23. Slip-bands in lead, showing four intersecting systems. 600 diameters, vertical light.

Fig. 24. Slip-bands in lead. 1000 diameters, vertical light. The photograph shows the straight slips and stepped intersections characteristic of this metal.

PLATE 22.

Fig. 25. Slip-bands in silver. Magnified 750 diameters, vertical light.

Fig. 26. Geometrical air-pits in glass-cast cadmium, slightly strained to show slip-bands. 1000 diameters, vertical light.

Fig. 27. Ditto.

PLATE 23.

Fig. 28. Ditto. See also remarks on Figs. 7, 8, and 9.

Fig. 29. Geometrical etched pits and slip-bands, produced by slight straining, in iron. 750 diameters, vertical light.

Fig. 30. Etched pits and slip-bands in iron. 1000 diameters, vertical light.

Fig. 31. Polished and etched section of cold-rolled Swedish iron. 45 diameters, oblique light, showing the differences of brightness on various grains and the uniform brightness over each individual grain.

PLATES 24 AND 25.

- Fig. 32. Distorted crystalline grains in a transverse section of cold-rolled Swedish iron, also showing geometrical etched pits. 200 diameters, vertical light.
- Fig. 33. A portion of the large distorted grain in Fig. 32, more highly magnified; the enlarged portion is at the angle of the distorted grain. 800 diameters, vertical light.
- Figs. 34, 35, and 36. Slip-bands in twin crystals of copper. 1000 diameters, vertical light.
- Fig. 37. Slip-bands in twin crystals of gold. 200 diameters, vertical light.
- Fig. 38. Slip-bands in twin crystals in gold. 45 diameters, oblique light.
- Fig. 39. Slip-bands in twin crystals of cold-hammered copper. 1000 diameters, vertical light.

PLATE 26.

- Fig. 40. Slip-bands in twin crystals observed in a specimen of plumbers' sheet-lead. 1000 diameters, vertical light.
- Fig. 41. Slip-bands and twinning in nickel. 1000 diameters, vertical light.
- Fig. 42. Elongated crystalline grains in cadmium cast on a sloping surface of glass. Transverse twin bands developed by slight straining are seen to run across a number of adjacent grains, with slight changes of direction on crossing a boundary. 100 diameters, vertical light.
- Fig. 43. Glass-cast surface of cadmium, showing double system of boundaries. 100 diameters, vertical light.

PLATES 27 AND 28.

- Fig. 44. High-power appearance of real and pseudo-boundaries as indicated by slip-bands. 1000 diameters, vertical light.
- Fig. 45. Strained mild-steel, showing "pearlite" patches and slips in "ferrite" areas. 1000 diameters, vertical light.
- Fig. 46. Glass-cast and etched surface of lead-tin eutectic. 750 diameters, vertical light.
- Figs. 47 and 48. Glass-cast and strained (but unetched) lead-tin eutectic. 750 diameters, vertical light.
- Fig. 49. Slowly-cooled lead-bismuth eutectic, etched and strained, showing slip-bands. 1000 diameters, vertical light.
- Figs. 50 and 51. Slip-bands in crystallites found in lead-bismuth alloy. 1000 diameters, vertical light.



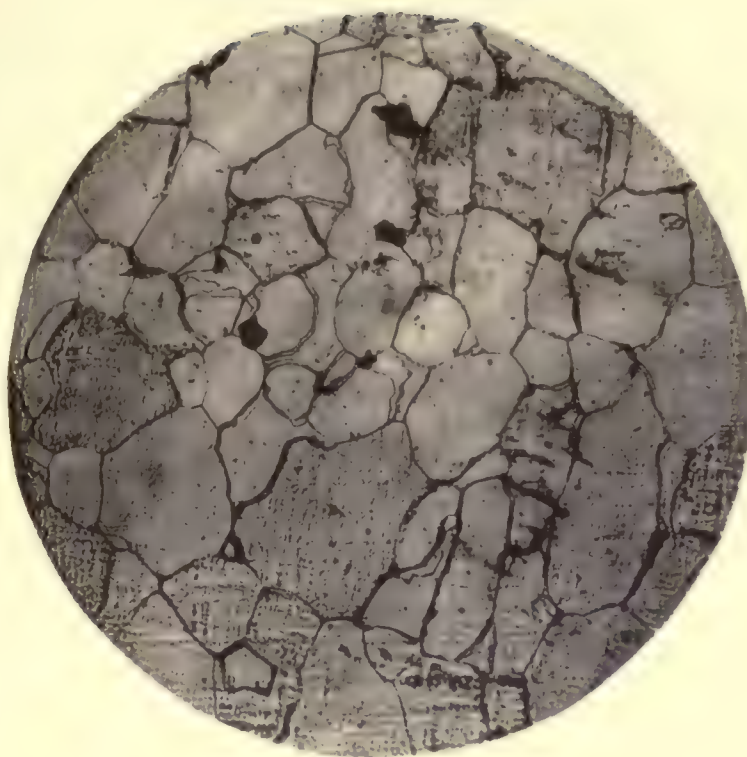


Fig. 2. IRON $\times 200$.

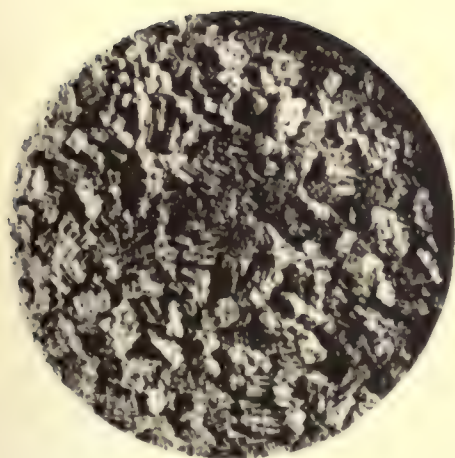


Fig. 3. BISMUTH $\times 3$.

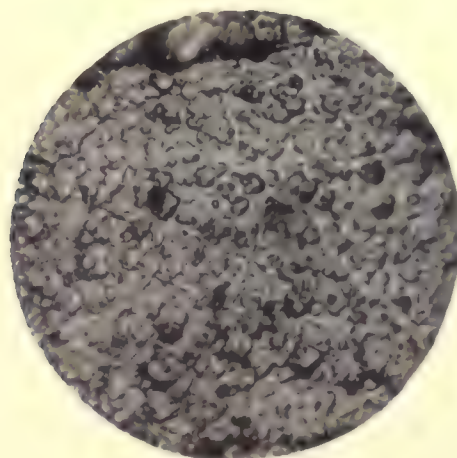


Fig. 4. IRON $\times 1500$.

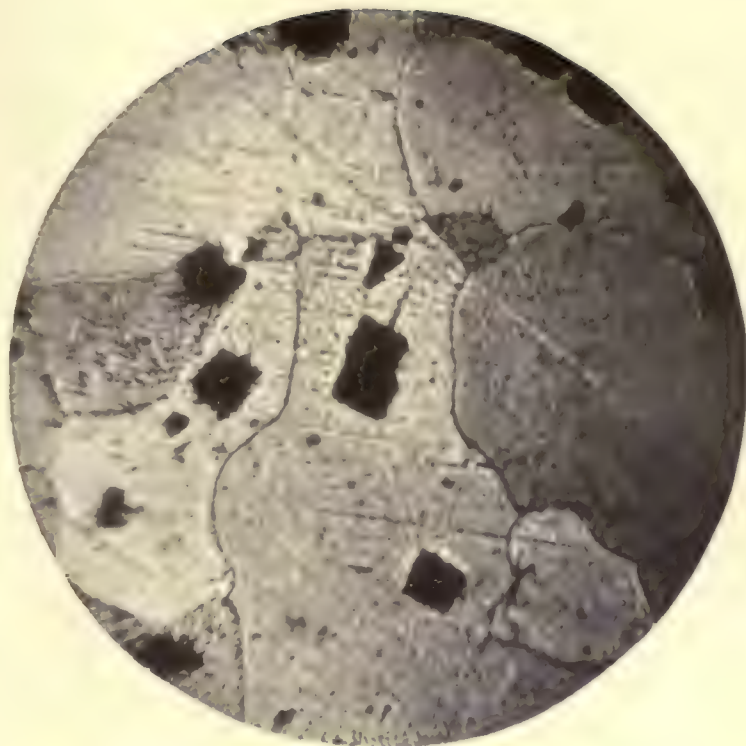


Fig. 5. IRON $\times 1000$.

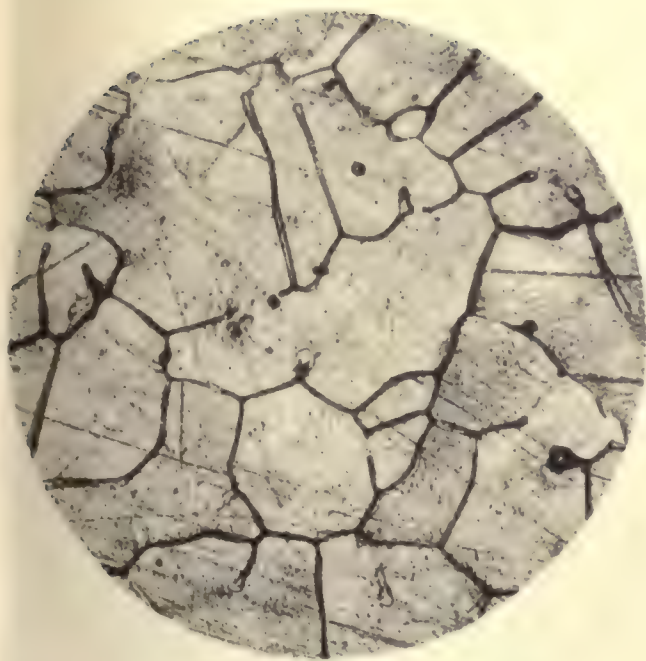


Fig. 6. CADMIUM $\times 100$.

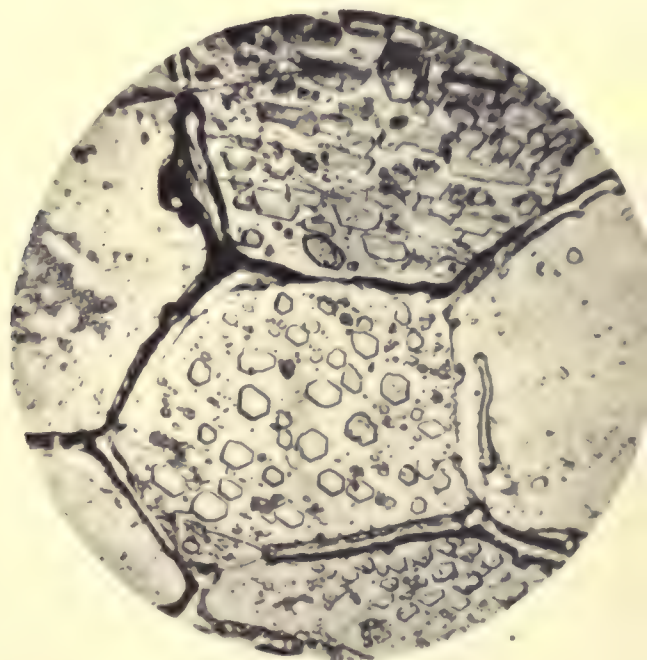


Fig. 7. CADMIUM $\times 1000$



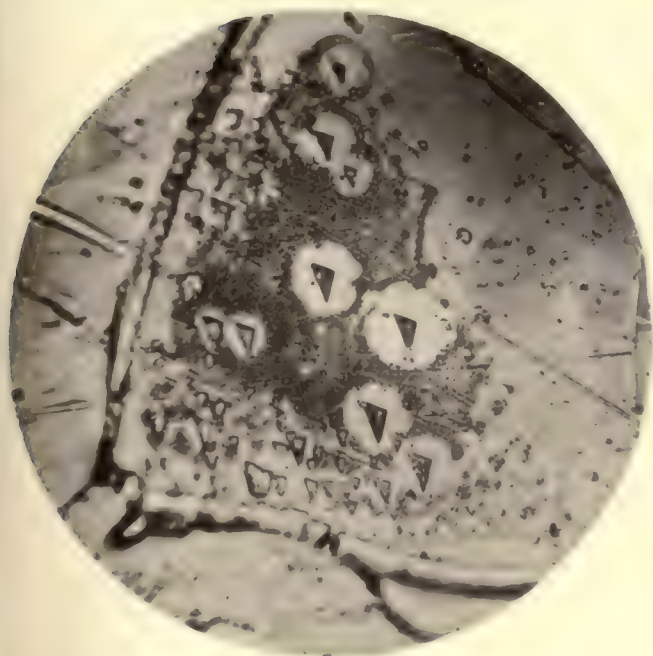


Fig. 8. CADMIUM $\times 1000$.

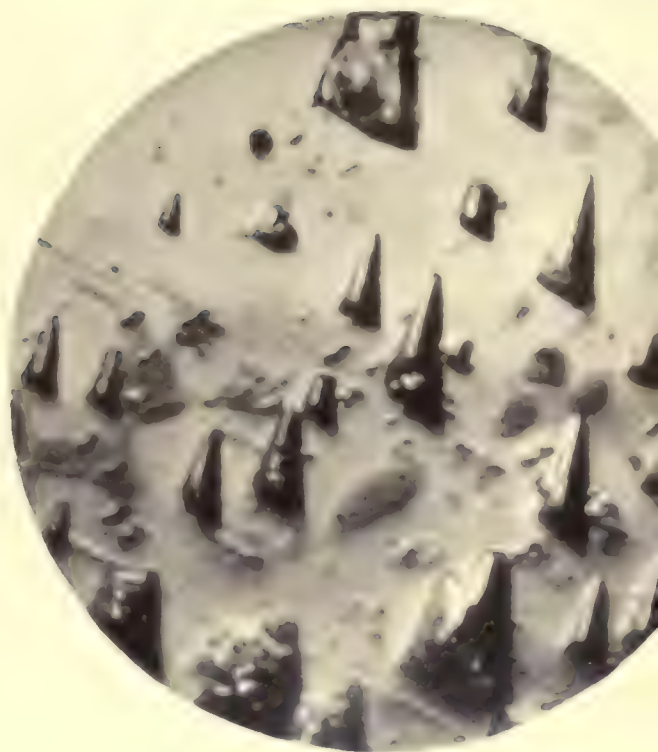


Fig. 9. CADMIUM $\times 4200$.

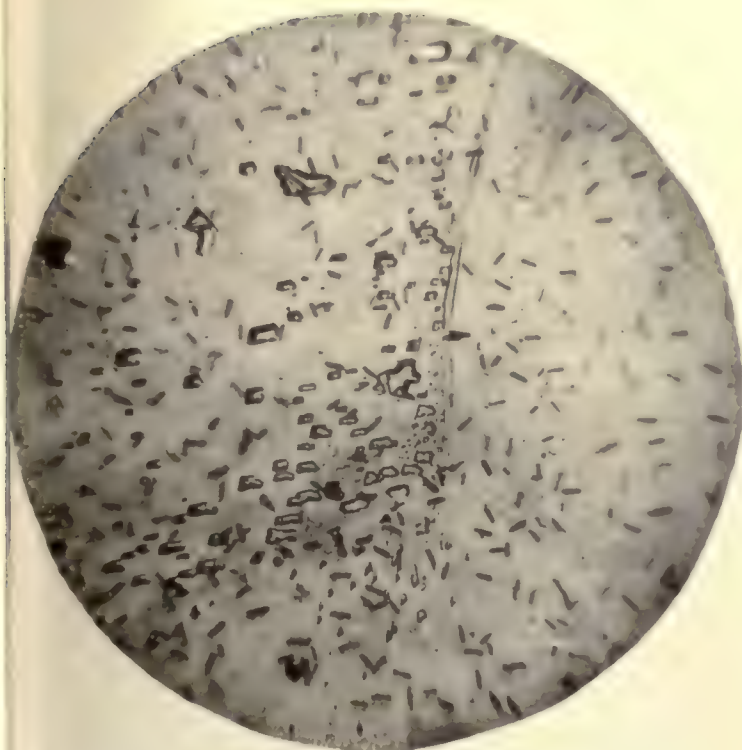


Fig. 10. TIN $\times 1000$.

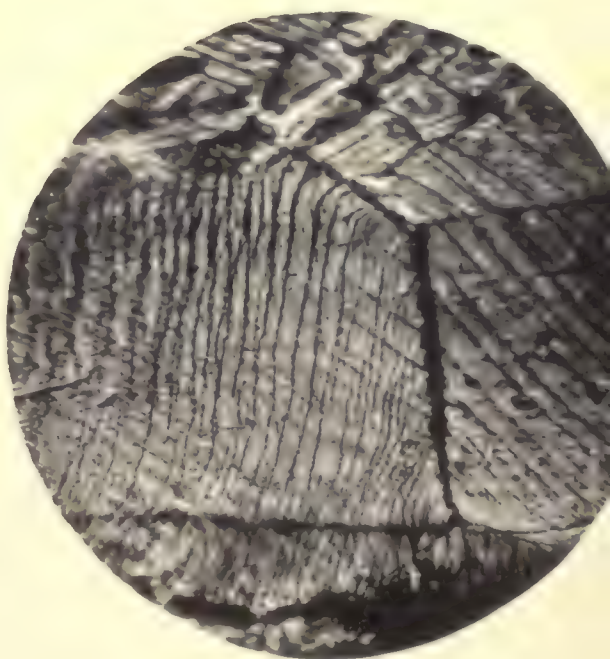


Fig. 12. IRON $\times 400$



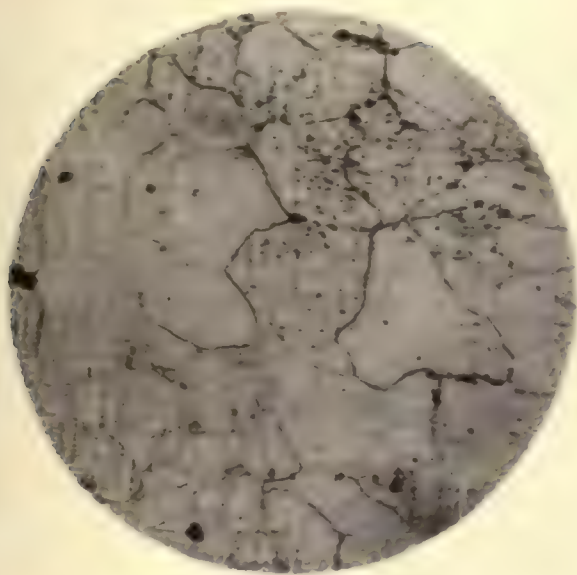


Fig. 13. IRON $\times 200$.

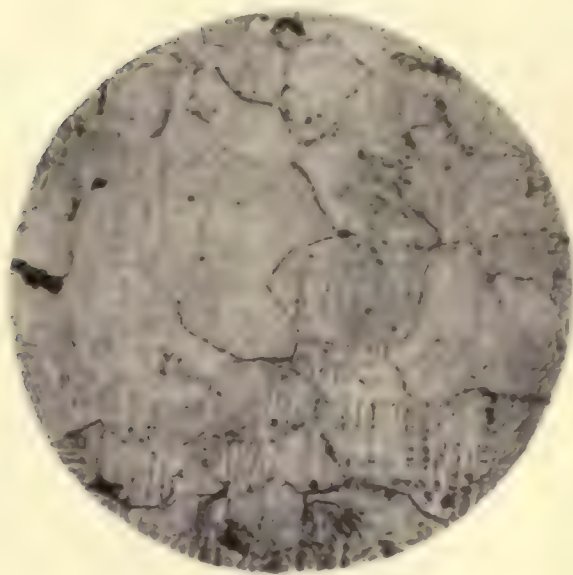


Fig. 14. IRON $\times 200$.

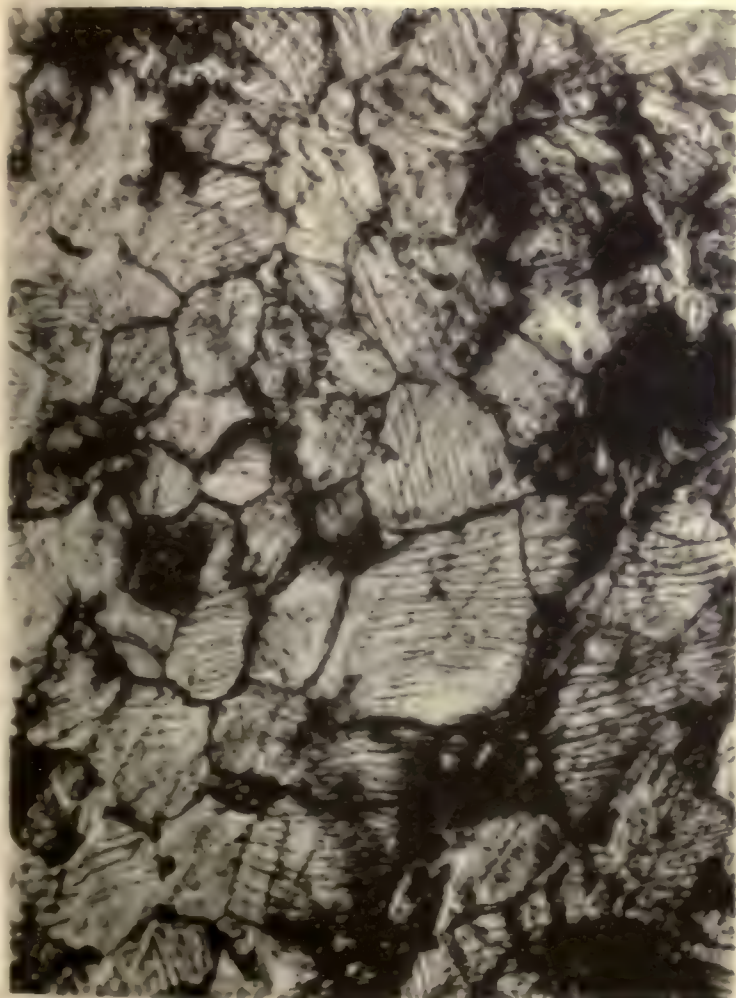




Fig. 18. LEAD $\times 100$.

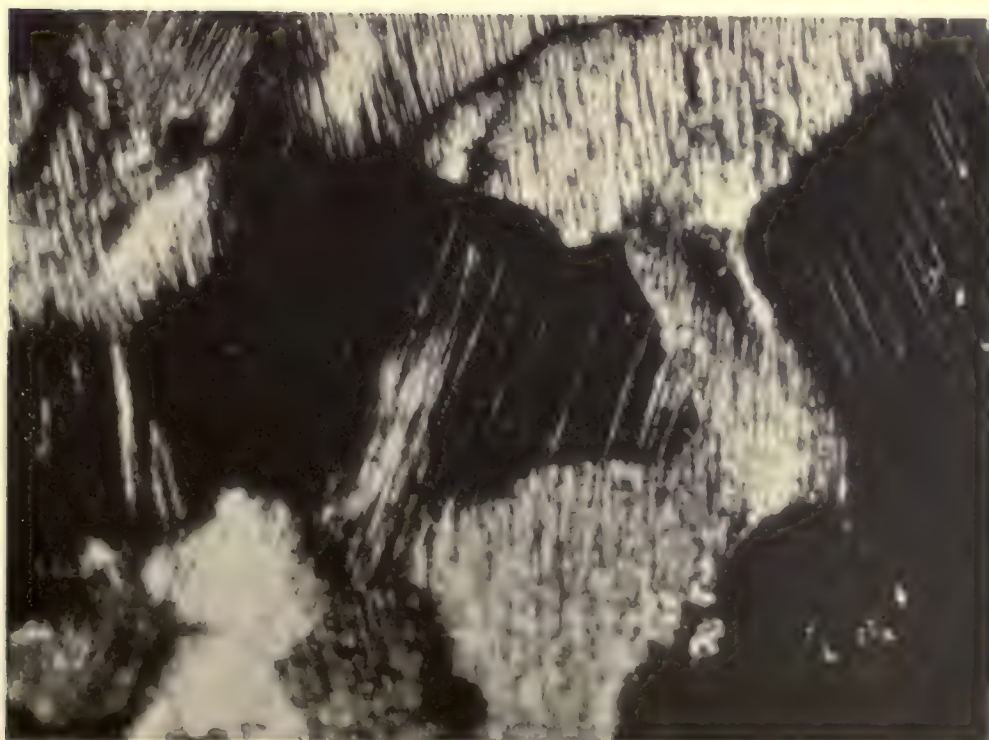


Fig. 19. LEAD $\times 100$.



Fig 20. LEAD $\times 100$.

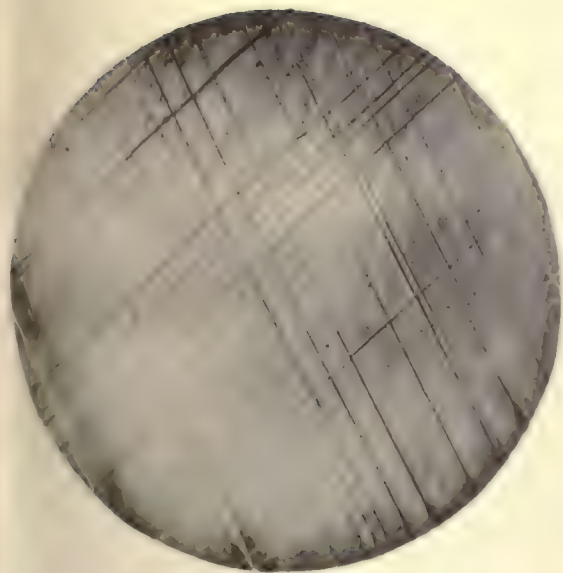


Fig. 23. LEAD $\times 600$.



Fig. 24. LEAD $\times 1000$.

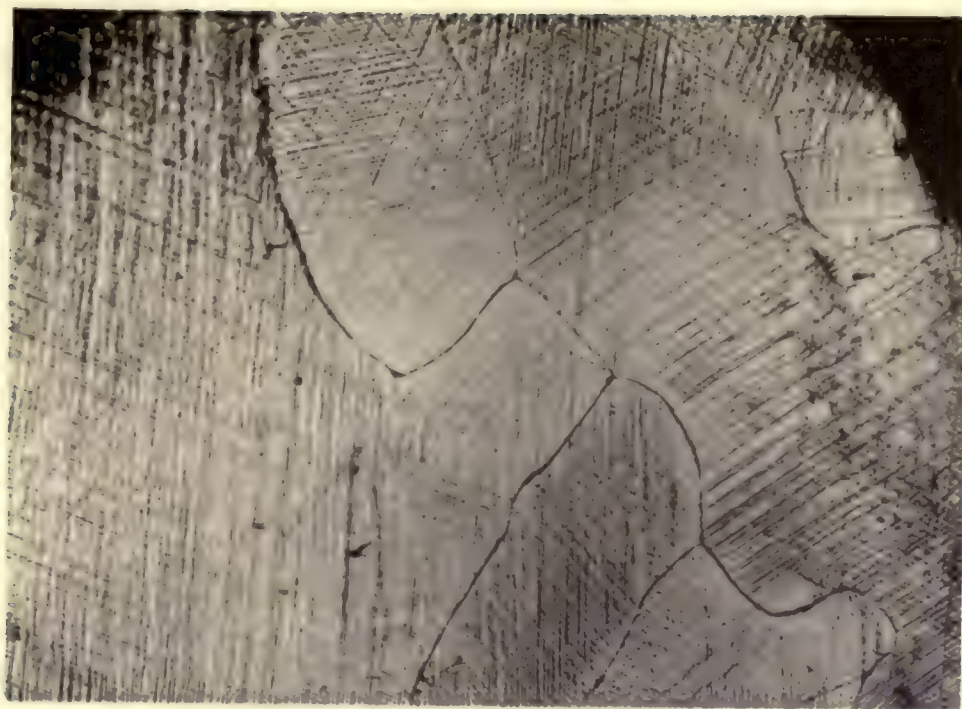


Fig. 21. LEAD $\times 100$.

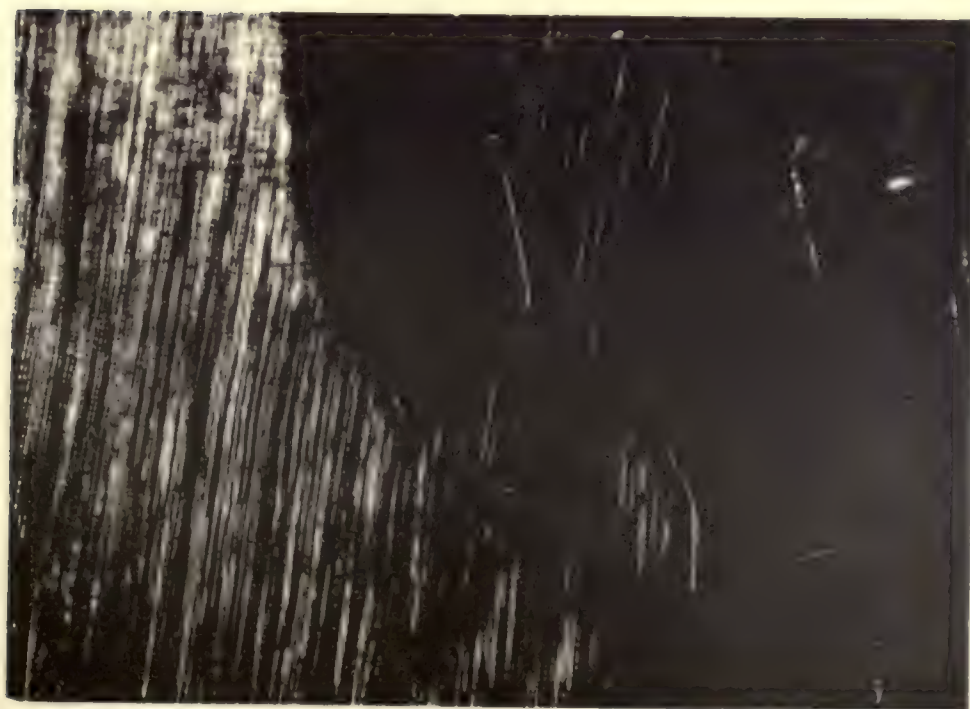


Fig. 22. LEAD $\times 100$

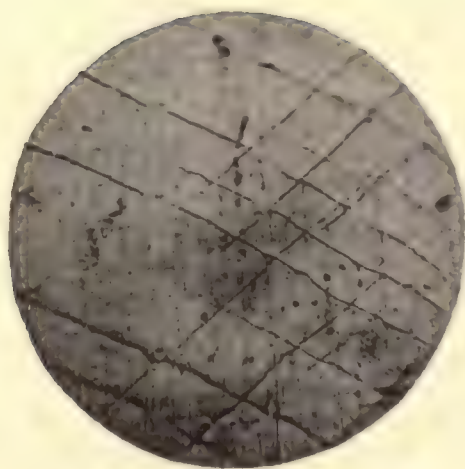


Fig. 25. SILVER $\times 750$.

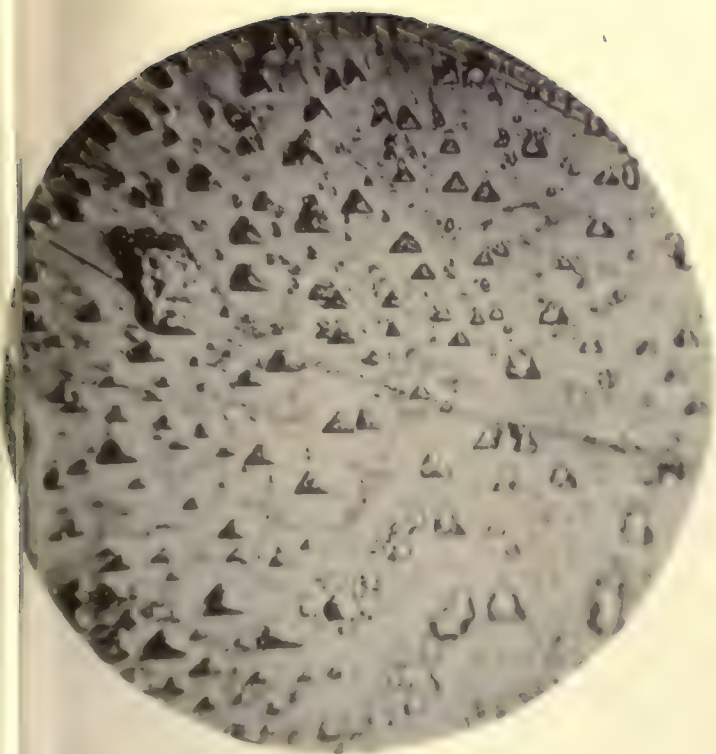


Fig. 26. CADMIUM $\times 1000$.

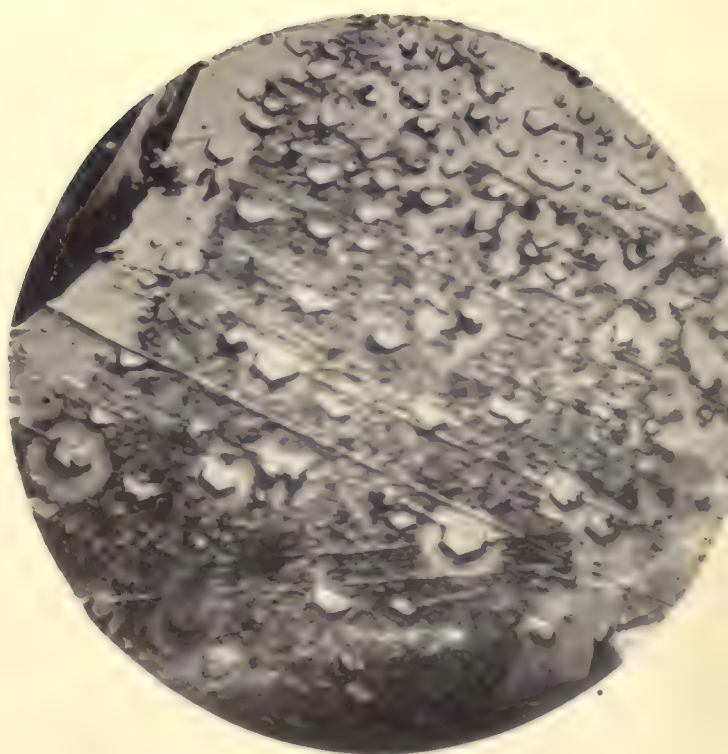


Fig. 27. CADMIUM $\times 1000$.



Fig. 28. CADMIUM $\times 1000$.

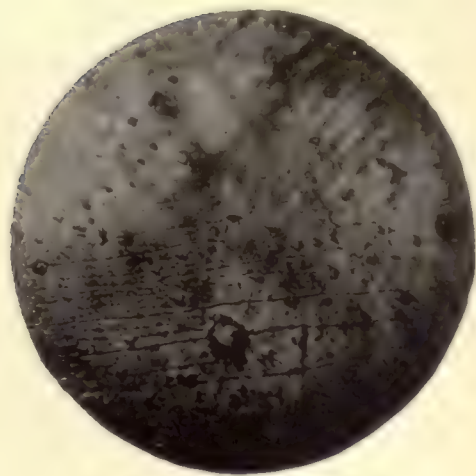


Fig. 29. IRON $\times 750$.

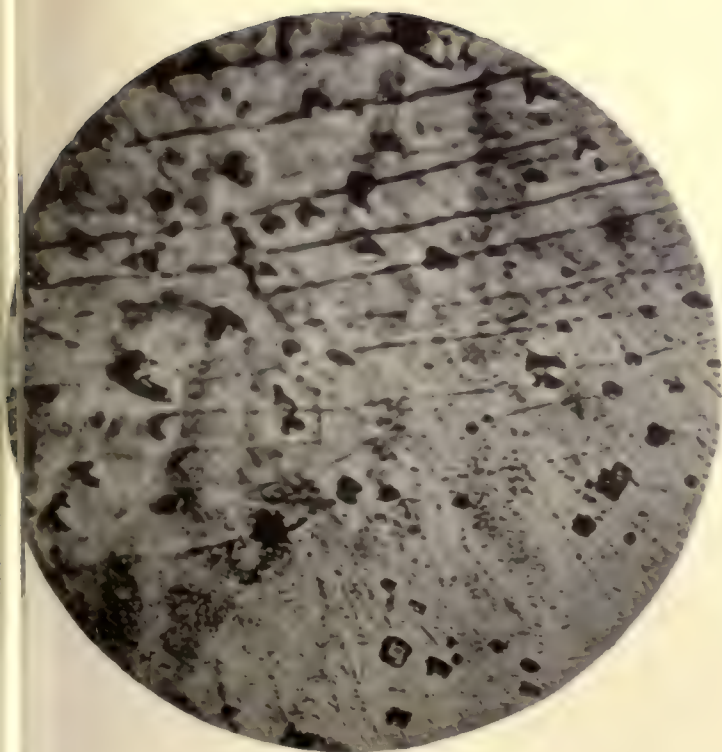


Fig. 30. IRON $\times 1000$.

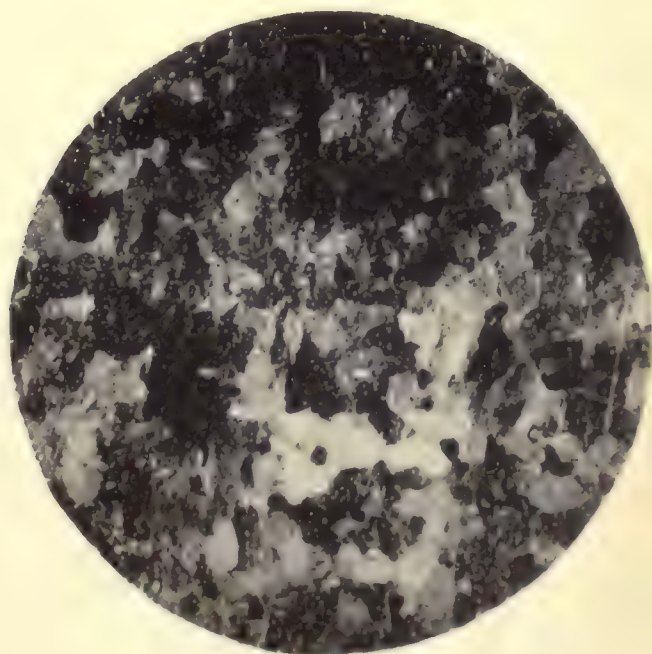


Fig. 31. IRON $\times 45$.

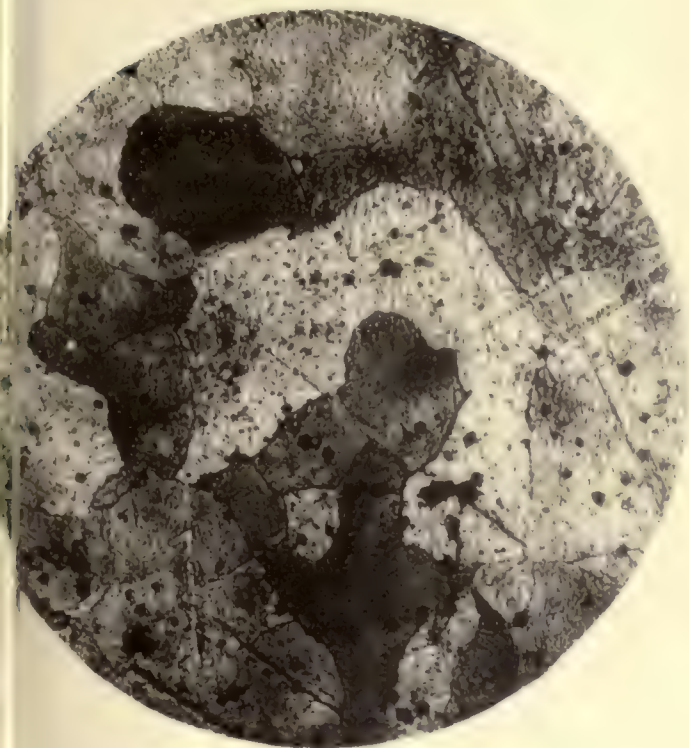


Fig. 32. IRON $\times 200$.

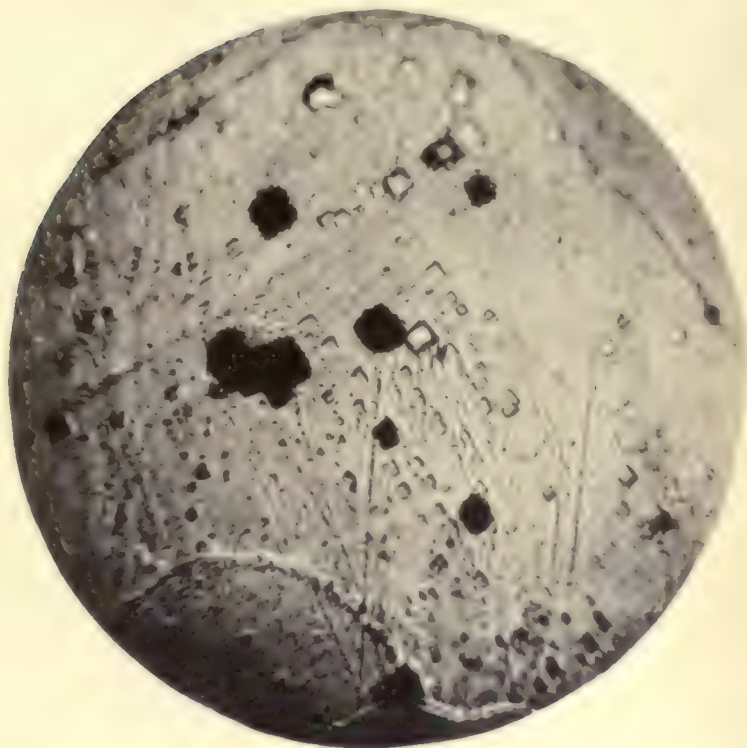


Fig. 33. IRON $\times 800$.



Fig. 34. COPPER $\times 1000$.

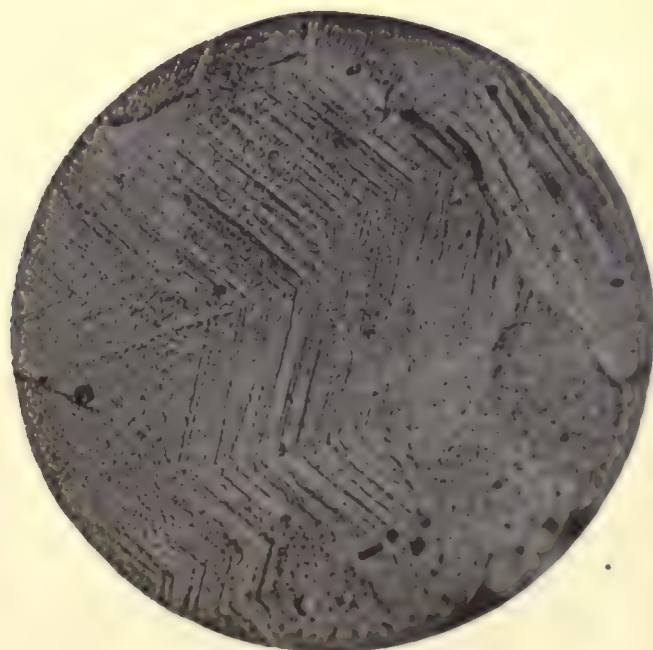


Fig. 35. COPPER $\times 1000$.



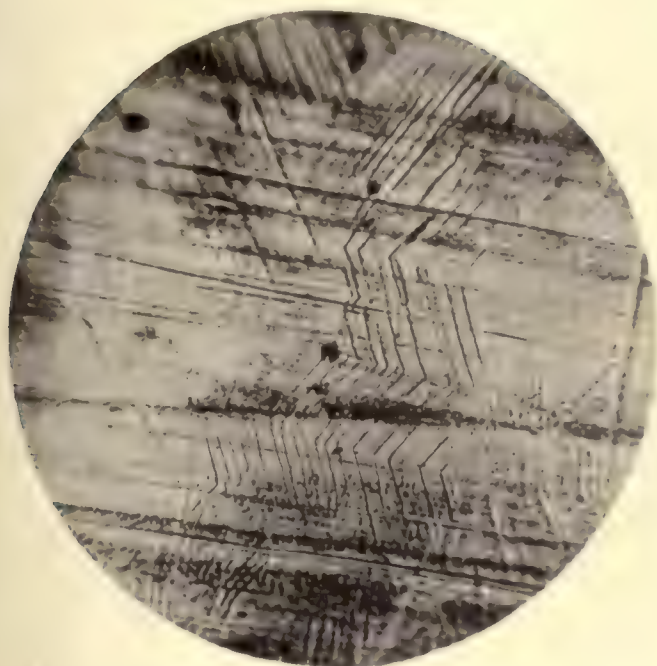


Fig. 36. COPPER $\times 1000$.



Fig. 37. GOLD $\times 200$.



Fig. 38. GOLD $\times 45$.



Fig. 39. COPPER $\times 1000$.



Fig. 40. LEAD $\times 1000$.

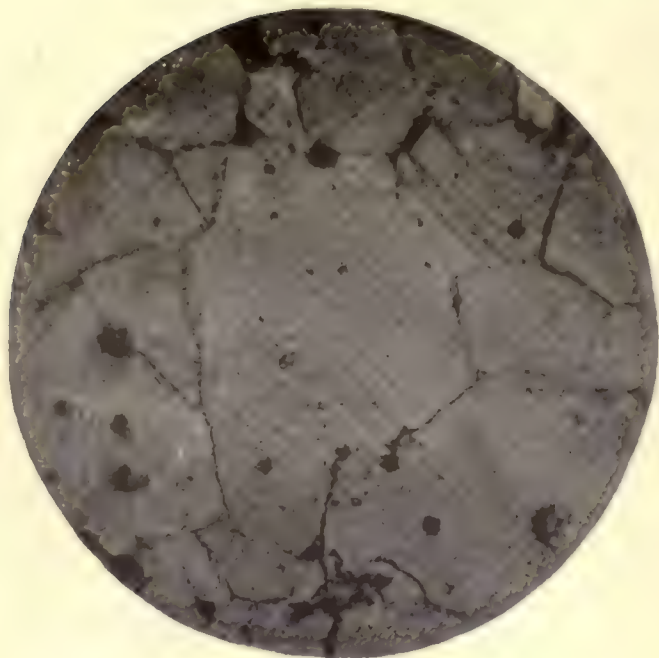


Fig. 41. NICKEL $\times 1000$.

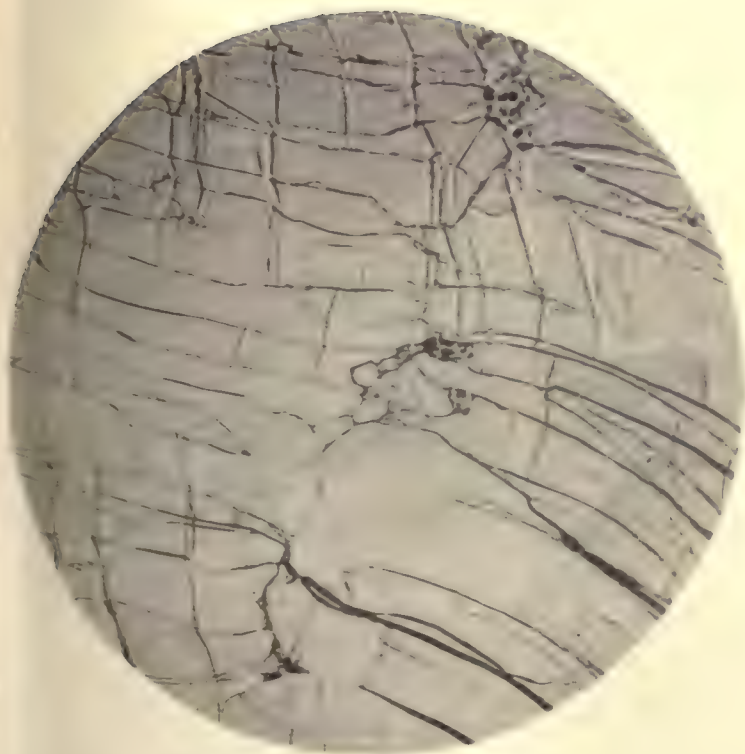


Fig. 42. CADMIUM $\times 100$.

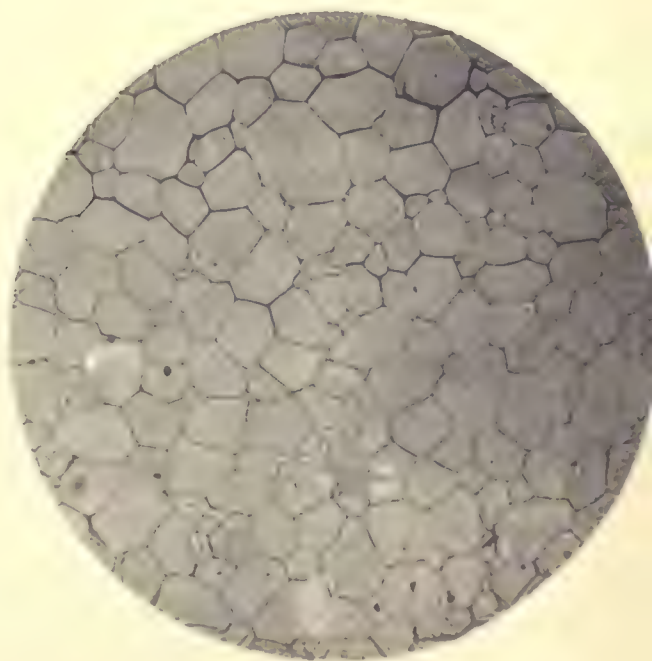


Fig. 43. CADMIUM $\times 100$.





Fig. 44. CADMIUM $\times 1000$.

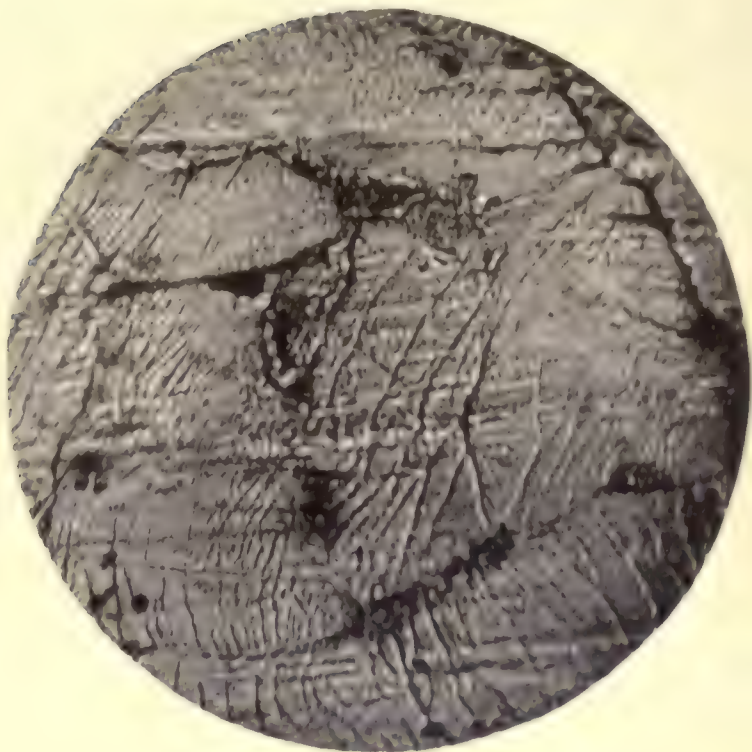


Fig. 45. MILD STEEL $\times 1000$.

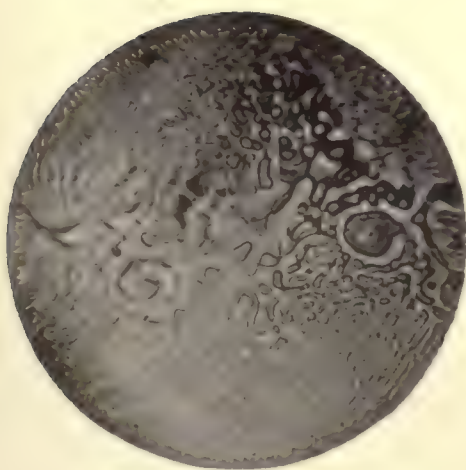


Fig. 46. LEAD-TIN EUTECTIC $\times 750$.



Fig. 47. LEAD-TIN EUTECTIC $\times 750$.



Fig. 48. LEAD-TIN EUTECTIC $\times 750$.



Fig. 49. LEAD-BISMUTH EUTECTIC $\times 1000$.

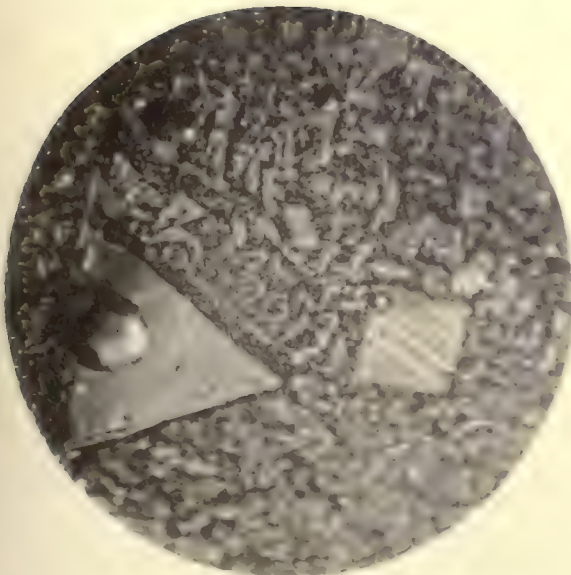


Fig. 50. LEAD-BISMUTH ALLOY $\times 1000$.



Fig. 51. LEAD-BISMUTH ALLOY $\times 1000$.

XII. *On the Least Potential Difference Required to Produce Discharge through Various Gases.*

By the Hon. R. J. STRUTT, B.A., Scholar of Trinity College, Cambridge.

Communicated by Lord RAYLEIGH, F.R.S.

Received October 17,—Read November 16, 1899.

Introduction.

MANY experimenters have made observations on the potential difference necessary to produce electric sparks through gases. The field is a very wide one, since the number of circumstances which may be varied is large. The nature and the pressure of the gas, the shape of the electrodes, the distance between them, and the pressure of the gas, may each be altered. The investigation of which I wish to give an account in this paper deals with the potential difference required to produce sparks (or *striking potential* as I shall call it for brevity) in various gases, between large parallel planes, at a fixed distance apart, and at various pressures.

It was found by Mr. PEACE ('Roy. Soc. Proc.,' vol. 52, p. 99) that the striking potential between two parallel plates in air diminished as the pressure diminished till a certain point was reached, and then began to rise very rapidly. The pressure at which the striking potential was a minimum depended on the distance between the plates, and increased as the distance was lessened. The minimum potential itself, however, varied very little with the distance between the plates.

This minimum potential was of the same order as the cathode fall of potential in air, as has been pointed out by Professor J. J. THOMSON ('Recent Researches in Electricity and Magnetism,' p. 158). The following explanation may be offered of the fact that this is a minimum striking potential, and that it is approximately constant.

The negative glow in any gas [as has been shown by WARBURG ('Wied. Ann.,' 31, p. 579)] requires for its production a definite potential difference (about 340 volts in the case of air), independent of the pressure, and constant, so long as the glow is not crushed into a smaller space than that which it would naturally occupy. If the glow is crushed, the potential fall is more. Let us now suppose that the discharge takes place between two parallel plates; a part of the space between these plates is occupied by the negative glow, a part by the positive column. So long as any of the

positive column remains it is clear that the negative glow is not constricted, and consequently it only requires 340 volts to produce it. The greater the length of the positive column the greater the corresponding potential difference; so that the striking potential will be the least possible when the pressure is low enough to make the negative glow occupy the whole space between the plates, but not low enough to make it require more space.

Although Mr. PEACE found the minimum striking potential to vary very little with the distance between the plates, and consequently very little with the pressure, yet the variation with the pressure was much greater than that observed by WARBURG for the cathode fall. WARBURG gives a table showing that a tenfold diminution in the pressure does not alter the cathode fall by 1 volt, *i.e.*, by $\frac{1}{2}$ per cent.

Mr. PEACE gives data showing a rise of 67 volts (20 per cent.) in the minimum striking potential.

It will thus be seen that, though there are theoretical reasons for thinking that the minimum striking potential should be equal to the cathode fall, the experimental evidence hitherto produced is scarcely sufficient to establish this relation. My experiments have been made with a view to determining the relation. The results will be discussed after the experimental arrangements have been described.

Description of Experimental Arrangements.

It was necessary to design the apparatus so as to require as little of the gas as possible, since it was intended to make some experiments on helium as well as on the common gases. The two brass plates of $1\frac{1}{2}$ inches diameter used as electrodes were embedded quite flush in ebonite plates 3 inches in diameter. The object of this was to prevent any tendency to sparking from the backs or edges of the brass discs. Three small ebonite distance pieces were placed between the brass plates, and the whole arrangement fastened together by means of three screws passing through the ebonite. Electrical connection to the brass plates was made by means of wires screwed into them, passing out axially through the ebonite.

The ebonite distance pieces were carefully measured before the apparatus was put together by means of a micrometer screw gauge. The lengths in millims. were:—

$$\begin{array}{ccc} \text{No. 1} \left\{ \begin{array}{l} 0.755 \\ 0.755 \end{array} \right. & \text{No. 2} \left\{ \begin{array}{l} 0.755 \\ 0.752 \end{array} \right. & \text{No. 3} \left\{ \begin{array}{l} 0.757 \\ 0.756 \end{array} \right. \end{array}$$

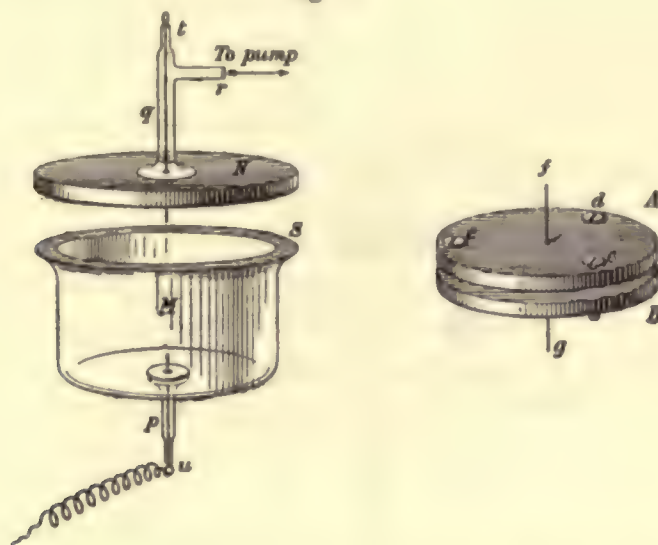
$$\text{Mean } 0.755 \text{ mm.} = 0.0297 \text{ inch.}$$

The brass plates being large compared with the distance between them, the electromotive intensity between them is sensibly uniform.

In order to be able to introduce various gases between the brass plates, and to vary the pressure, it was necessary to enclose them in an air-tight chamber,

The arrangement is represented in fig. 1. A, B, are the ebonite discs, into the fronts of which the brass sparking plates are let. These latter are not visible in the figure. The ebonite plates are held together by the three screws *c*, *d*, *e*. The small distance between them is equal to the thickness of the distance pieces. The leading wires pass to the plates at *f* and *g*.

Fig. 1.



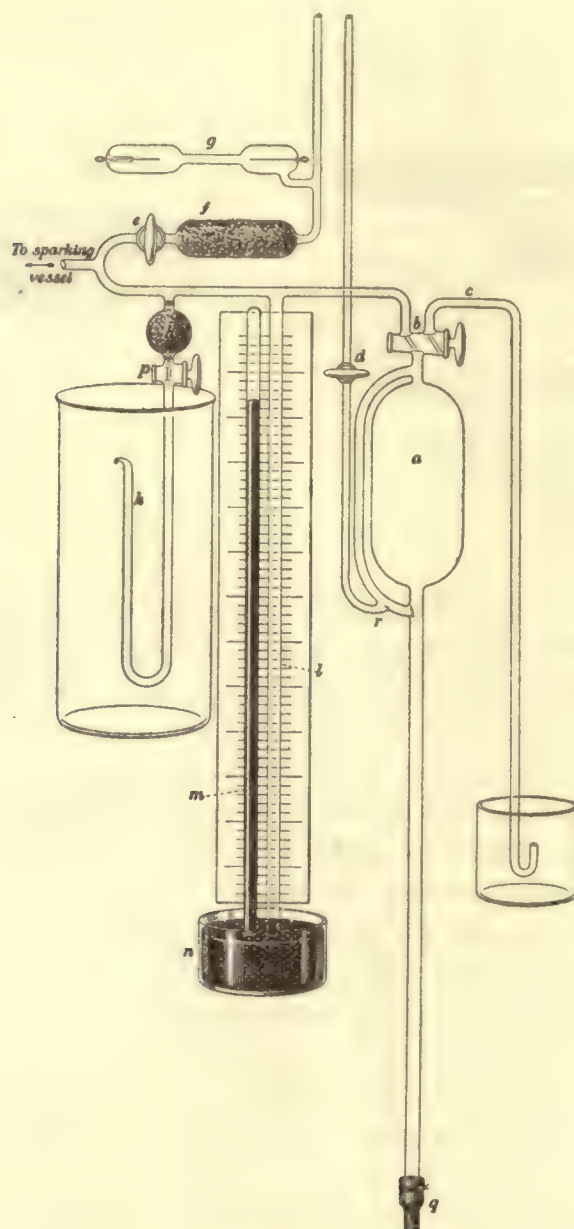
This whole arrangement is enclosed in the cylindrical glass pot M, shown separately for the sake of clearness. M has a broad ground flange S, which is covered by the glass lid N, the joint being made tight with sealing wax. The leads are introduced through holes drilled in the middle of the lid and the bottom of the pot. Over these holes are placed the glass tubes *p*, *q*, up which the wires pass. These tubes have flanges at the ends, ground flat so as to fit the flat surface to which they are cemented. A side tube *r* provides the means of admitting and withdrawing gas. The wires are fused through the tube at *t* and *u*.

In order conveniently to vary the pressure and adjust it to any desired value, it was necessary to provide a reservoir into which the gas could be drawn, or from which it could be expelled, by raising or lowering a mercury vessel. It was also necessary to provide a means of exhausting the apparatus. A special form of mercury pump was designed, by means of which both these objects could be attained. By thus dispensing with a separate reservoir, the apparatus was considerably simplified.

The pump is shown in fig. 2. The general arrangement of the various parts will, it is hoped, be sufficiently clear from the figure. *a* is the pump, which also serves for the adjustment of the pressure in the manner to be presently described. *g* is a vacuum tube, which serves for observing the spectrum of the gas as a test of its purity. *f* and *h* are phosphoric anhydride drying tubes. *d* and *e* and *p* are ordinary

glass stopcocks. *b* is a three-way glass stopcock. *l* is the manometer tube. A barometer tube, *m*, is arranged by the side of it, and dips into the same mercury vessel *n*. The height of the mercury columns in these tubes can be read off to the $\frac{1}{10}$ th of a millim. on the mirror glass scale behind them. The difference of these heights, of course, gives the pressure of gas in the apparatus.

Fig. 2.



k is a U-shaped tube immersed in a glass beaker, and serves for the introduction of gas into the apparatus. Before filling with gas, it is necessary to remove the air from the sparking vessel.

For this purpose stopcocks *d* and *e* are opened, and *b* is set so as to open communication between *a* and *c*. The mercury reservoir (not shown) attached to the india-rubber hose *q* is raised. Mercury rises in *a*, driving out the air through *c*, and on lowering the mercury, fresh air bubbles in at *r*, just as in the ordinary Toepler pump. When the apparatus has been exhausted, stopcocks *d* and *e* are shut. *b* is turned so as to open communication between *a* and *r*, and gas is admitted through *p* to any desired pressure. The pressure can then be varied at pleasure by raising or lowering the mercury in *a*. The mercury reservoir attached to the hose *q* can be fixed at any given height so as to make the mercury stand at a corresponding height in *a*. The object of shutting off the part between the stopcocks *d* and *e* is to make the volume in connection with *a* as small as possible, thus making it possible to obtain a greater range of pressure without admitting or removing gas permanently. Another advantage of this contrivance was that, when helium was to be used, less of it would be required. The volume required to fill the apparatus to atmospheric pressure was only about 40 cc., when *a* was entirely filled with mercury.

We now come to the arrangements for producing and measuring the striking potential. A large Wimshurst machine was used. It was driven at a constant speed by means of an electric motor. The potential difference between its terminals was measured by means of one of Lord KELVIN'S multicellular electrostatic voltmeters. This instrument has been checked by Mr. CAPSTICK. He compared it with a quadrant electrometer standardised by Clark cells, and found it practically correct. I have also verified it to some extent myself, by observing the *additional* deflection produced by 50 volts, this latter voltage being determined by a Weston voltmeter, believed to be trustworthy. No measurable discrepancy was detected.

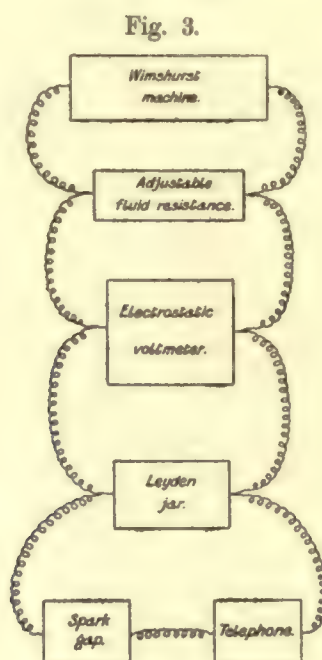
Some previous experimenters have used a Wimshurst machine in direct connection with the spark terminal, and have turned it till the spark passed. This method succeeds fairly well when large spark lengths and, consequently, large spark potentials are to be measured. But when the spark potential is small it is scarcely possible to raise the potential slowly enough to prevent the needle of the instrument swinging violently; and if this occurs, it is of course impossible to make any accurate observations. PEACE (*loc. cit.*) failed to get consistent measurements with the Wimshurst machine. He was driven to the use of a battery of storage cells. The use of these, however, very much adds to the trouble of the investigation, and I was able to avoid it in the following manner. The machine was shunted by means of a fluid high resistance column of variable length. When running at a constant speed the difference of potential at the terminals of the resistance column was constant, and depended of course on the length of the resistance column in use. By gradually increasing the amount of this resistance the potential difference could be raised to any desired value and adjusted with the utmost nicety.

In order further to improve the electrical steadiness of the arrangement a large

Leyden jar was also connected across the terminals of the machine. The capacity thus added diminished the effect of any slight irregularities in its action.

It is not easy to observe the faint sparks which pass between the sparking plates unless the observer gives his undivided attention to watching for them, and if this be done it is impossible to read the potential difference at the exact moment when the spark takes place. A telephone was therefore inserted in series with the spark gap, and arranged in a clip so as to be against the observer's ear when his eye was in the proper position for reading the voltmeter. Whenever a spark passed, the telephone gave an easily audible click. By means of these arrangements the measurements could be taken with considerable rapidity and precision.

A diagram (fig. 3) of the electrical connections is given below.



It must be remembered that the first spark taken through a gas passes with far greater difficulty than those which succeed it. I have found a gas able to sustain for a short time a potential difference three times as great as that required to produce discharge through it when this initial resistance had been broken down. If the measurements of the spark potential are to be compared with the cathode fall measurements made while a continuous current was flowing through the gas, it is clear that they should be made with the gas in its electrically weakest condition, that is, immediately after it has been vigorously sparked through. This condition was complied with in my experiments.

In taking a measurement of the spark potential, the pressure of the gas was adjusted to the desired value and read off. The machine was started, and the resistance column lengthened until the potential rose sufficiently to cause the first spark to

pass. This first spark was followed by a torrent of others, the telephone emitting a chattering noise. The resistance column was gradually shortened until these sparks ceased, and then cautiously lengthened until they just began again.

At the moment when this happened the voltmeter was read. The voltage was allowed to rise slowly enough to prevent any appreciable swing of the needle.

When an observation had been taken, the voltage was again reduced below the sparking value, and then again cautiously increased by lengthening the resistance column. When the telephone began to click the reading was again noted. Ten observations were usually taken at each pressure. They could be obtained in fairly rapid succession.

Experiments on Atmospheric Air.

The first set of measurements was made on atmospheric air, not specially well dried.

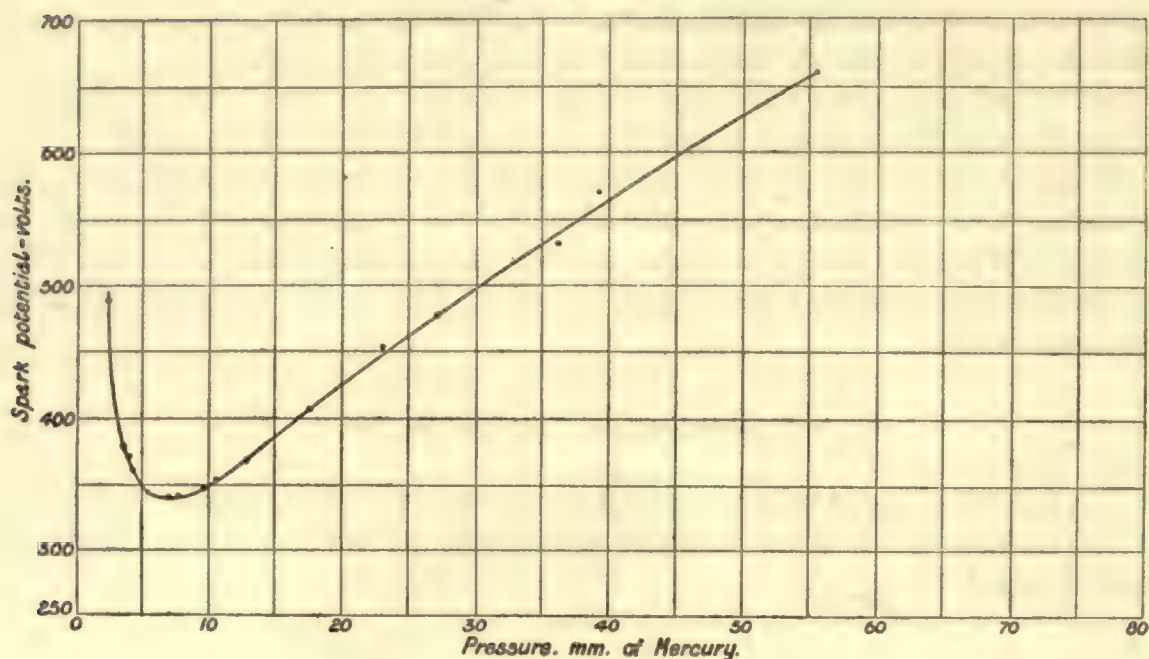
The readings will be given in full, as an example, to show the degree of concordance obtained.

Pressure (mm.) of mercury.	Spark potential (volts).	Mean value of spark potential.
72.4	800, 780, 760, 740, 740, 760, 780, 770, 770, 770 . .	767
55.6	640, 650, 665, 650, 660, 667, 662, 680, 670, 660 . .	660
39.1	570, 580, 555, 578, 580, 572, 563, 575, 560, 565 . .	570
36.1	540, 530, 520, 550, 510, 520, 520, 540, 525, 550 . .	531
27.2	470, 470, 466, 470, 490, 475, 485, 480, 484, 485, 468 .	477
23.1	461, 460, 458, 440, 462, 459, 451, 432, 457, 455 . .	454
17.5	410, 413, 421, 402, 405, 400, 412, 409, 407, 405 . .	408
13.1	370, 376, 360, 370, 359, 358, 380, 375, 365, 375 . .	369
10.7	350, 351, 358, 360, 353, 360, 350, 352, 353 . .	354
9.6	355, 345, 348, 340, 349, 350, 351, 345, 350, 347 . .	348
7.9	341, 339, 341, 342, 342, 340, 341, 341, 346 . .	341
7.0	342, 348, 330, 350, 340, 339, 339, 340, 343, 336 . .	341
5.4	345, 347, 343, 340, 348, 346, 347, 347, 345, 341 . .	345
4.4	360, 362, 362, 361, 365, 365, 360, 365, 355, 360 . .	362
4.0	370, 372, 380, 372, 372, 375, 365, 364, 375, 375 . .	372
3.8	372, 380, 380, 380, 381, 385, 380, 380, 380, 378 . .	380
2.4	500, 490, 483, 483, 502, 480, 470, 487, 500, 483 . .	488
1.8	755, 800, 780, 790, 790, 770, 790, 800, 780, 760 . .	782

The minimum spark potential is thus 341 volts. It will be noticed that the larger potential differences, *i.e.*, those furthest on either side from the minimum, could not be measured with the precision that was possible with those in the neighbourhood of the minimum. As, however, the value of the minimum is the point of chief interest, this is of small importance.

The results are plotted on Diagram No. 1. The smoothness of the curve is some guarantee of the accuracy of the observations.

Diagram No. 1.—Air.

*Hydrogen.*

We now come to the experiments on hydrogen. The hydrogen was prepared first by the electrolysis of caustic potash solution, and dried by means of phosphoric anhydride. The sample of gas thus prepared gave a minimum spark potential of 300 volts. The readings were as follows:—

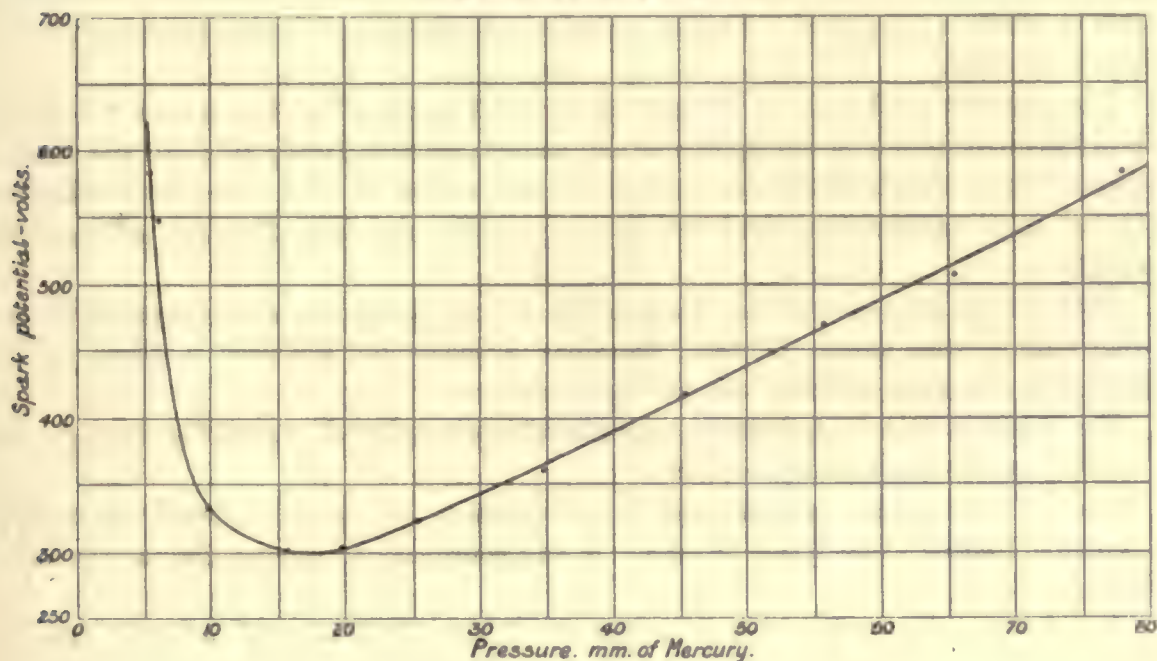
Pressure (mm.).	Spark potential (volts.)
90.9	589
78.0	584
65.5	507
55.8	470
45.4	416
34.8	360
25.1	323
19.9	303
15.5	302
9.9	333
6.0	548
5.4	583

These results are plotted on Diagram No. 2.

It will be seen that the minimum is very nearly 300 volts.

In order to check this result a sample of hydrogen was used which had been occluded by palladium foil. This gave results in close agreement with the above, the minimum spark potential being 308 volts.

Diagram No. 2.—Hydrogen.



Nitrogen.

This gas is extremely troublesome to deal with. Although each sample tried gave smooth curves for the relation between the spark potential and the pressure, yet no agreement could be obtained between different samples of the gas, even though they were prepared in the same way and with the greatest care I was able to bestow.

Thus, for example, a specimen of nitrogen prepared from air by absorption of the oxygen with alkaline pyrogallol gave for the minimum 347 volts.

A sample from ammonium nitrite purified by passage through caustic potash and sulphuric acid and over phosphoric anhydride gave 351 volts.

Another sample prepared in the same way and dried with especial care, by being allowed to stand in contact with phosphoric anhydride all night, gave 369 volts.

A sample prepared by the removal of oxygen from air by means of metallic copper gave 388 volts.

Although these values for the minimum spark potential vary so widely, yet the rate of change of the spark potential with the pressure, at pressures well above that corresponding to the minimum, was approximately the same in all the samples.

My experience with the nitrogen is entirely in accord with that of WARBURG. He

found that the cathode fall in ordinary nitrogen was extremely inconstant. Thus in one case the value of this quantity, at first 315 volts, gradually rose to 410 volts during the passage of the current for many hours. He found that this variation in the value of the cathode fall was connected with the presence of traces of oxygen in the nitrogen—traces too small to be removed by the ordinary chemical absorbents, such as alkaline pyrogallol. I was anxious to try whether the same cause was operative in my case.

The method employed by WARBURG for getting rid of the last traces of oxygen from his nitrogen was to transport metallic sodium electrolytically through the heated glass of his discharge tube, so as to form a clean surface of that metal on the inside. At the high temperature used the sodium rapidly absorbed all traces of residual oxygen.

Such a method was obviously inapplicable to my apparatus, put together as it was with sealing wax joints. I used, therefore, a somewhat different method, which, though troublesome to carry out, gave good results.

This method was to bubble the sample of gas employed repeatedly through the liquid alloy of sodium and potassium.

The alloy must be manipulated in the absence of air to prevent its surface becoming fouled. The vessel in which it was contained is represented in the next figure.

a and *b* are glass bulbs blown on the side limbs of a Y-shaped tube *f*. On the bottom limb of this Y there is a stopcock *g*. The lower part of the limb is of capillary bore.

The bulbs *a* and *b* can be placed in communication by means of the stopcock *c*. *d* and *e* are bulbs containing phosphoric anhydride to constitute an additional safeguard against the access of moisture to the alloy. The exit tubes from these bulbs lead respectively to the pump-reservoir and to the sparking vessel.

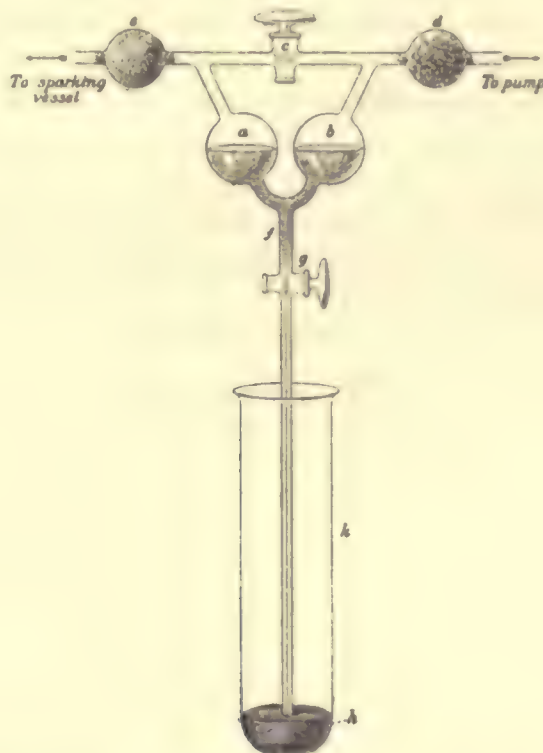
The alloy was prepared in a test-tube *k*, by melting some sodium and adding potassium until the product remained liquid on cooling. A few drops of rock oil were from time to time placed on the surface of the alloy. The vapour from this sufficiently guarded against the access of air.

To introduce the alloy into the apparatus, *c* was opened and *g* closed. The air was then pumped out from the system of tubes.

The test-tube containing the alloy was then brought up as shown in the figure, the end *h* of the Y being *under the surface* of the alloy. *g* was then cautiously opened so that the alloy was sucked up into the bulbs *a* and *b*. When it had risen about half-way up them, as shown in the figure, *g* was closed, thus preventing the entry of any more of the alloy. In this way the alloy could be introduced without any contamination. It had all the appearance of clean mercury. This apparatus was used to absorb traces of oxygen from nitrogen in the following way:—*c* being open and in communication with the pump reservoir, the gas was admitted. *c* was then

closed. On allowing the mercury to rise in the pump reservoir, the gas in the bulb *b* was compressed, and forced the surface of the alloy down to *f*. The gas then bubbled up through the bulb *a*, and was compressed into the sparking vessel. When the mercury reservoir was lowered again, the gas bubbled back again through the alloy, now in the bulb *b*.

Fig. 4.



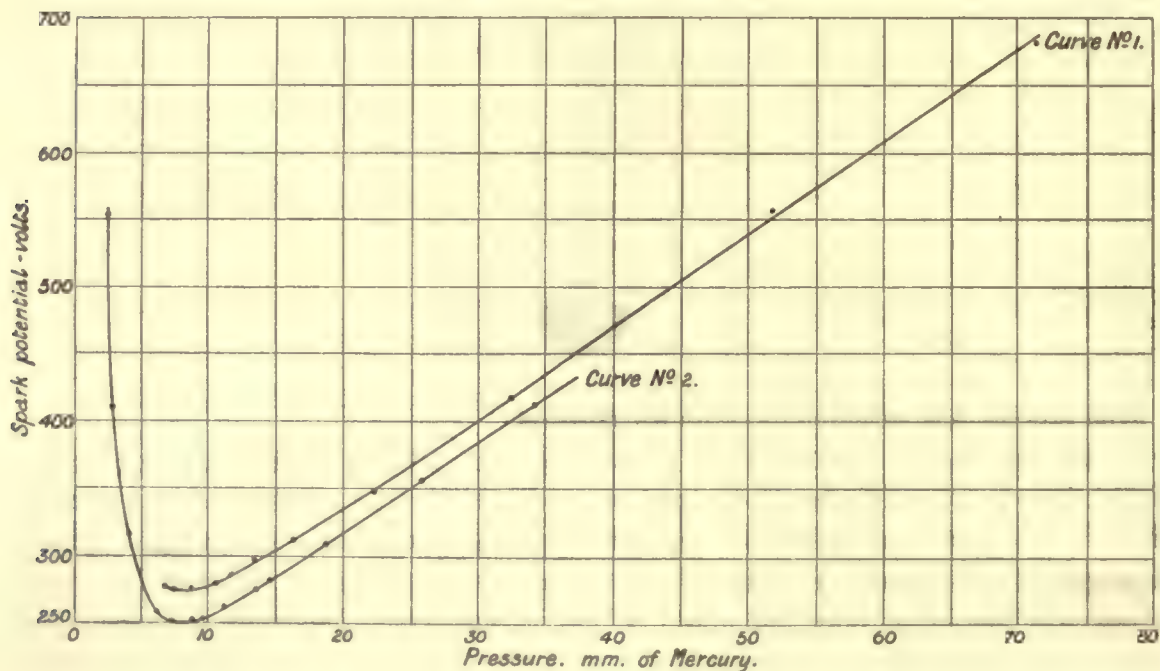
This process was repeated as often as required.

It was not possible to pass *all* the gas through the alloy at each operation; yet by giving time for the diffusion of the gas compressed into the sparking vessel, so as to allow it to become of uniform composition throughout, before being again passed through the absorbent, a very efficient purification could be effected by a few passages of the gas through the alloy. When as much had been drawn into the pump reservoir as circumstances allowed, the amount remaining behind in the sparking vessel was not more than one-fifth of the whole. Thus, supposing all the oxygen to be taken out of that part of the gas which had actually bubbled through the alloy, only $\frac{1}{5}$ would remain after the first operation, $\frac{1}{25}$ after the second, $\frac{1}{125}$ after the third, and so on.

When it was desired to measure the spark potential in the purified gas, the tap *c* was opened, so as to make the pressure the same in the manometer as in the sparking vessel. If this had not been done, the pressure due to the column of alloy would

have destroyed the equality of these pressures. The nitrogen employed was prepared by the action of heat on ammonium nitrite. Ammonium chloride solution was contained in a flask, fitted with an india-rubber cork, through which passed a dropping funnel and an exit tube for the gas. Potassium nitrite solution was contained in the funnel, and could be dropped into the warmed ammonium chloride. The gas passed through strong sulphuric acid and caustic potash solutions, each contained in ordinary potash bulbs. From these it passed into a chamber containing phosphoric anhydride, closed at either end by taps. An approximate vacuum was first made in the entire arrangement by means of a water pump. This reduced the pressure to something less than a centimetre of mercury. Gas was then liberated so as to slowly fill the apparatus up to atmospheric pressure. A current was allowed to flow for some time through the phosphoric anhydride chamber, so as to wash out all traces of air. When this had been done the chamber was shut off, and the gas left in it all night, so that it might become thoroughly dry. It could then be admitted through a tap into the sparking vessel.

Diagram No. 3.—Nitrogen.



After the gas had been passed several times through the alloy, the following measurements were taken (Diagram No. 3, curve 1):—

Pressure (mm.).	Voltage.
71.1	683
51.7	559
32.4	418
22.2	348
16.2	311
13.5	298
11.7	287
10.6	280
8.9	276
7.6	276
6.8	279

It will be seen that the minimum was about 276 volts—much lower than the values obtained with nitrogen not specially treated.

The treatment with the alloy was now continued for some hours.

The following set of readings was obtained after this :—

Pressure (mm.).	Voltage.
34.2	411
25.8	356
18.9	308
14.6	281
13.8	275
11.1	262
9.8	251
8.9	251
7.3	251
6.0	259
4.0	315
2.9	410
2.3	553

Further treatment with the alloy did not appreciably reduce the minimum voltage.

A repetition of this experiment with a fresh sample of nitrogen gave a result in close agreement with the above. The minimum may be therefore taken as 251 volts.

It will be seen that the perfect removal of oxygen does not much affect the slope of the curve in its straight part, where the pressure is above the critical value. The interpretation of this (on the view given above) is that the cathode fall of potential, not that near the anode, is affected by the presence of traces of oxygen.

Helium.

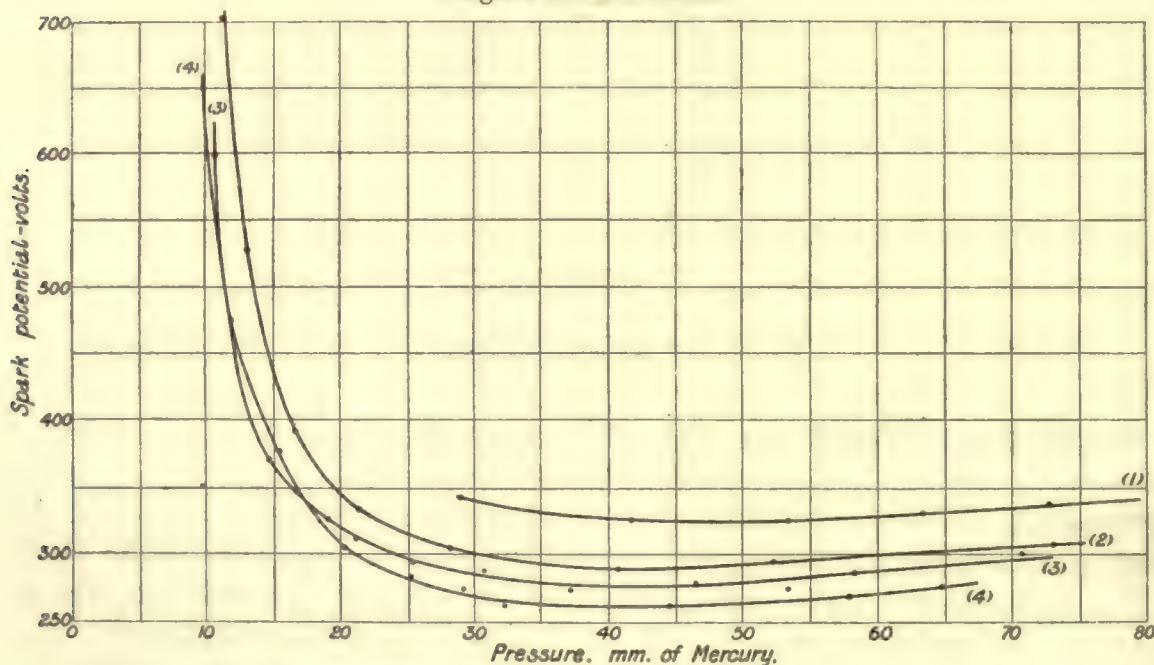
It has been shown by Professor RAMSAY and Dr. COLLIE ('Roy. Soc. Proc.' vol. 59, p. 259) that helium at atmospheric pressure allows sparks to pass through it much

more easily than does air. With a given E.M.F. ten times as long a spark was obtained in helium as in air. This is a very striking result. It seemed, therefore, well worth while to investigate the behaviour of helium as regards its spark potential in the same way as the other gases.

For the method of preparing this gas I must refer to a paper "On the Discharge of Electricity through Argon and Helium," which I hope shortly to publish, where it is described in detail. I merely state here that it was extracted from monazite by means of strong sulphuric acid, and that nitrogen and other impurities were removed from it by mixing with oxygen and exposing it to the action of electric sparks in presence of caustic alkali. The oxygen was then removed by suitable absorbents.

Although all the care I was able to give was spent on the purification of the gas, some cause, the nature of which remains a mystery, made the spark potential variable. It was found that if a specimen of helium remained in the apparatus, and measurements of its spark potential were taken at intervals, the value of this quantity went down. As an example of this, I will give a series of measurements made on a sample of helium from which the surplus oxygen had been removed by the copper-ammonia method of HEMPEL.*

Diagram No. 4.—Helium.



Any gaseous ammonia which might remain in the helium was removed by means of dilute sulphuric acid. The helium was dried by phosphoric anhydride, and examined

* This method consists in bringing the gas into contact with metallic copper at the ordinary temperature, the copper having just been washed free from oxide by a solution of ammonia to which some ammonium carbonate has been added. See HEMPEL, 'Methods of Gas Analysis,' p. 126.

spectroscopically. No trace of nitrogen bands could be seen. The red hydrogen line was visible, as it always is in a vacuum tube. This sample of gas gave the following readings when first put into the apparatus :—

1.

Pressure (mm.).	Voltage.
94.0	348
83.1	340
72.8	339
63.5	332
53.5	326
41.9	326
29.0	343

Minimum 326.

The gas was left in the apparatus untouched. Next day the readings obtained were :—

2.

Pressure (mm.).	Voltage.
91.7	341
73.0	309
52.3	295
40.9	288
28.1	303
21.5	332
16.5	391
13.2	528
11.3	703

Minimum 288.

The gas was again left untouched till next morning :—

3.

Pressure (mm.).	Voltage.
81.9	316
70.7	301
58.1	285
46.5	280
37.2	274
30.8	288
25.4	294
21.2	311
19.2	326
1.48	370
1.09	599

Minimum 274.

It will thus be seen that, after the gas has been sparked through, its sparking potential is lowered. In this case the minimum was lowered from 326 to 288, and then to 274.

To see what the effect of further sparking would be, a torrent of sparks was passed through the gas by means of the machine for an hour. The readings then taken were :—

4.

Pressure (mm.).	Voltage.
64.9	276
57.9	269
44.8	261
32.3	261
29.2	274
25.2	284
20.3	303
15.6	377
12.0	475
10.0	650

Minimum 261.

It will be seen that the minimum has gone down still further. Another three hours' sparking did not make any further difference. The minimum spark potential after this treatment was 262 volts, practically the same as before. Other specimens of helium from which the surplus oxygen had been removed by means of phosphorus (at the ordinary temperature) behaved very similarly.

It may be remarked that this behaviour of helium is very like that observed by **WARBURG** in the case of nitrogen which had not been put through any exceptional treatment for the removal of its surplus oxygen : with this difference, however, that he found the cathode fall go up (from 315 to 410 volts) with the sparking, whereas, in my measurements on helium, the spark potential went down.

It seems not unlikely that if the last traces of oxygen were removed from the helium by means of the sodium-potassium alloy, normal and constant results might be obtained. I hope to examine this point on some future occasion.

General Conclusions.

It remains to discuss the results obtained, and to inquire how far they bear out the conclusion that the minimum spark potential is equal to the cathode fall measured over the whole extent of the negative glow in a vacuum tube.

For this purpose it will be convenient to tabulate the values of these quantities for the various gases side by side.

Nature of gas.	Cathode fall given by Warburg.	Minimum spark potential found above
Atmospheric air	340-350 volts ('Wied. Ann.,' vol. 31, p. 559) .	volts. 341
Hydrogen	About 300 volts ('Wied. Ann.,' vol. 31, p. 581) .	302, 308
Ordinary nitrogen, carefully dried	Varies 315-410 (" " " p. 557) .	347, 351 369, 388
Nitrogen specially freed from all traces of oxygen	230 volts ('Wied. Ann.,' vol. 40, p. 1)	251
Helium	[Values found by myself (see paper on "Discharge of Electricity through Argon and Helium"). 226 volts.]	Varies 326-261

In the case of air, the agreement is as good as could be expected, and, indeed, much better. It is also satisfactory in the case of hydrogen.

In ordinary nitrogen the results are in neither case constant. But my numbers all lie between the extremes found by WARBURG.

In the specially purified nitrogen a difference of about 10 per cent. is to be observed. For measurements of this kind the discrepancy is not enough to establish an essential want of equality. It is possible that my method of removing oxygen, which depended on the use of alkali metals at ordinary temperatures, was not quite so efficient as that of WARBURG, who used a high temperature.

In the case of helium alone is the value of the cathode fall seriously different from that of the minimum spark potential.

Although this discrepancy is large, I do not think that, in view of the satisfactory agreement in the other cases, it can be considered to weigh seriously against the equality. It must be remembered that the values found for helium differ much more among themselves than the lowest of them differs from the measured cathode fall. Measurements of the same quantity which do not agree with one another cannot be expected to agree with other independent measurements.

I think it may be considered to be established by these experiments that the minimum spark potential is equal to the cathode fall.

One point is very strikingly brought out by the curves. I mean the extremely small rate of increase of the spark potential with the pressure in the case of helium, and the relatively high pressure at which the minimum occurs. All the features shown by the curves for the common gases are seen in the curve for helium, but the difference in degree is very striking. The enormous length of spark at atmospheric pressure in helium as compared with air might almost suggest that the conduction is

effected in some radically different way. But these curves show that the behaviour of helium when conveying the discharge, though very peculiar, is not radically different from that of the common gases.

In conclusion, I must record my best thanks to Professor J. J. THOMSON. I cannot adequately express how much I owe to his kind encouragement and advice.

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CONTAINING PAPERS OF A MATHEMATICAL OR PHYSICAL CHARACTER.

VOL. 194.

LONDON:

PRINTED BY HARRISON AND SONS, ST. MARTIN'S LANE, W.C.

Printers in Ordinary to Her Majesty.

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THE Committee appointed by the *Royal Society* to direct the publication of the *Philosophical Transactions* take this opportunity to acquaint the public that it fully appears, as well from the Council-books and Journals of the Society as from repeated declarations which have been made in several former *Transactions*, that the printing of them was always, from time to time, the single act of the respective Secretaries till the Forty-seventh Volume; the Society, as a Body, never interesting themselves any further in their publication than by occasionally recommending the revival of them to some of their Secretaries, when, from the particular circumstances of their affairs, the *Transactions* had happened for any length of time to be intermitted. And this seems principally to have been done with a view to satisfy the public that their usual meetings were then continued, for the improvement of knowledge and benefit of mankind: the great ends of their first institution by the Royal Charters, and which they have ever since steadily pursued.

But the Society being of late years greatly enlarged, and their communications more numerous, it was thought advisable that a Committee of their members should be appointed to reconsider the papers read before them, and select out of them such as they should judge most proper for publication in the future *Transactions*; which was accordingly done upon the 26th of March, 1752. And the grounds of their choice are, and will continue to be, the importance and singularity of the subjects, or the advantageous manner of treating them; without pretending to answer for the certainty of the facts, or propriety of the reasonings contained in the several papers so published, which must still rest on the credit or judgment of their respective authors.

It is likewise necessary on this occasion to remark, that it is an established rule of the Society, to which they will always adhere, never to give their opinion, as a Body,

upon any subject, either of Nature or Art, that comes before them. And therefore the thanks, which are frequently proposed from the Chair, to be given to the authors of such papers as are read at their accustomed meetings, or to the persons through whose hands they received them, are to be considered in no other light than as a matter of civility, in return for the respect shown to the Society by those communications. The like also is to be said with regard to the several projects, inventions, and curiosities of various kinds, which are often exhibited to the Society ; the authors whereof, or those who exhibit them, frequently take the liberty to report, and even to certify in the public newspapers, that they have met with the highest applause and approbation. And therefore it is hoped that no regard will hereafter be paid to such reports and public notices ; which in some instances have been too lightly credited, to the dishonour of the Society.

1900.

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Genoa.

p. Società Ligustica di Scienze Naturali e Geografiche.

Milan.

AB. Reale Istituto Lombardo di Scienze, Lettere ed Arti.

AB. Società Italiana di Scienze Naturali.

Modena.

p. Le Stazioni Sperimentali Agrarie Italiane.

Naples.

p. Società di Naturalisti.

AB. Società Reale, Accademia delle Scienze.

B. Stazione Zoologica (Dr. DOHRN).

Padua.

p. University.

Palermo.

A. Circolo Matematico.

AB. Consiglio di Perfezionamento (Società di Scienze Naturali ed Economiche).

A. Reale Osservatorio.

Pisa.

p. Il Nuovo Cimento.

p. Società Toscana di Scienze Naturali.

Rome.

p. Accademia Pontificia de' Nuovi Lincei.

p. Rassegna delle Scienze Geologiche in Italia.

Italy (continued).**Rome (continued).**

A. Reale Ufficio Centrale di Meteorologia e di Geodinamica, Collegio Romano.

AB. Reale Accademia dei Lincei.

p. R. Comitato Geologico d' Italia.

A. Specola Vaticana.

AB. Società Italiana delle Scienze.

Siena.

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p. Laboratorio di Fisiologia.

AB. Reale Accademia delle Scienze.

Venice.

p. Ateneo Veneto.

AB. Reale Istituto Veneto di Scienze, Lettere ed Arti.

Japan.**Tokiô.**

AB. Imperial University.

p. Asiatic Society of Japan.

Java.**Buitenzorg.**

p. Jardin Botanique.

Luxembourg.**Luxembourg.**

p. Société des Sciences Naturelles.

Malta.

p. Public Library.

Mauritius.

p. Royal Society of Arts and Sciences.

Netherlands.**Amsterdam.**

AB. Koninklijke Akademie van Wetenschappen.

p. K. Zoologisch Genootschap 'Natura Artis Magistra.'

Delft.

p. École Polytechnique.

Haarlem.

AB. Hollandsche Maatschappij der Wetenschappen.

p. Musée Teyler.

Leyden.

AB. University.

Rotterdam.

AB. Bataafsch Genootschap der Proefondervindelijke Wijsbegeerte.

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New Zealand.**Wellington.**

AB. New Zealand Institute.

Norway.**Bergen.**

AB. Bergenske Museum.

Christiania.

AB. Kongelige Norske Frederiks Universitet.

Tromsøe.

p. Museum.

Trondhjem.

AB. Kongelige Norske Videnskabers Selskab.

Portugal.**Coimbra.**

AB. Universidade.

Lisbon.

AB. Academia Real das Sciencias.

p. Secção dos Trabalhos Geologicos de Portugal.

Oporto.

p. Annaes de Sciencias Naturaes.

Russia.**Dorpat.**

AB. Université.

Irkutsk.

p. Société Impériale Russe de Géographie (Section de la Sibérie Orientale).

Kazan.

AB. Imperatorsky Kazansky Universitet.

p. Société Physico-Mathématique.

Kharkoff.

p. Section Médicale de la Société des Sciences Expérimentales, Université de Kharkoff.

Kieff.

p. Société des Naturalistes.

Kronstadt.

p. Marine Observatory.

Moscow.

AB. Le Musée Public.

B. Société Impériale des Naturalistes.

Odessa.

p. Société des Naturalistes de la Nouvelle Russie.

Pulkowa.

A. Nikolai Haupt-Sternwarte.

St. Petersburg.

AB. Académie Impériale des Sciences.

B. Archives des Sciences Biologiques.

AB. Comité Géologique.

AB. Ministère de la Marine.

A. Observatoire Physique Central.

Scotland.**Aberdeen.**

AB. University.

Edinburgh.

p. Geological Society.

p. Royal College of Physicians (Research Laboratory).

Scotland (continued).

Edinburgh (continued).

- p. Royal Medical Society.
- A. Royal Observatory.
- p. Royal Physical Society.
- p. Royal Scottish Society of Arts.
- AB. Royal Society.

Glasgow.

- AB. Mitchell Free Library.
- p. Natural History Society.
- p. Philosophical Society.

Servia.

Belgrade.

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Sicily. (See ITALY.)

Spain.

Cadiz.

- A. Instituto y Observatorio de Marina de San Fernando.

Madrid.

- p. Comisión del Mapa Geológico de España.
- AB. Real Academia de Ciencias.

Sweden.

Gottenburg.

- AB. Kongl. Vetenskaps och Vitterhets Samhälle.

Lund.

- AB. Universitet.

Stockholm.

- A. Acta Mathematica.
- AB. Kongliga Svenska Vetenskaps-Akademie.
- AB. Sveriges Geologiska Undersökning.

Upsala.

- AB. Universitet.

Switzerland.

Basel.

- p. Naturforschende Gesellschaft.

Bern.

- AB. Allg. Schweizerische Gesellschaft.
- p. Naturforschende Gesellschaft.

Geneva.

- AB. Société de Physique et d'Histoire Naturelle.
- AB. Institut National Genevois.

Lausanne.

- p. Société Vaudoise des Sciences Naturelles.

Neuchâtel.

- p. Société des Sciences Naturelles.

Zürich.

- AB. Das Schweizerische Polytechnikum.
- p. Naturforschende Gesellschaft.
- p. Sternwarte.

Tasmania.

Hobart.

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Albany.

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Austin.

- p. Texas Academy of Sciences.

Baltimore.

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Berkeley.

- p. University of California.

Boston.

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- B. Boston Society of Natural History.
- A. Technological Institute.

Brooklyn.

- AB. Brooklyn Library.

Cambridge.

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Chapel Hill (N.C.).

- p. Elisha Mitchell Scientific Society.

Charleston.

- p. Elliott Society of Science and Art of South Carolina.

Chicago.

- AB. Academy of Sciences.
- p. Astrophysical Journal.
- p. Field Columbian Museum.

Davenport (Iowa).

- p. Academy of Natural Sciences.

Granville (Ohio).

- p. Journal of Comparative Neurology.

Ithaca (N.Y.).

- A. Journal of Physical Chemistry.
- p. Physical Review (Cornell University).

Lawrence.

- p. Kansas University.

Madison.

- p. Wisconsin Academy of Sciences.

Mount Hamilton (California).

- A. Lick Observatory.

New Haven (Conn.).

- AB. American Journal of Science.
- AB. Connecticut Academy of Arts and Sciences.

New York.

- p. American Geographical Society.
- A. American Mathematical Society.
- p. American Museum of Natural History.
- AB. Columbia College Library.
- p. New York Academy of Sciences.
- p. New York Medical Journal.

United States(continued).

Philadelphia.

- AB. Academy of Natural Sciences.
- AB. American Philosophical Society.
- p. Franklin Institute.
- p. Wagner Free Institute of Science.

Rochester (N.Y.).

- p. Academy of Science.

St. Louis.

- p. Academy of Science.

Salem (Mass.).

- p. American Association for the Advancement of Science.

- AB. Essex Institute.

San Francisco.

- AB. California Academy of Sciences.

United States (continued).

Washington.

- AB. Patent Office.
- AB. Smithsonian Institution.
- AB. United States Coast Survey.
- E. United States Commission of Fish and Fisheries.
- AB. United States Geological Survey.
- AB. United States Naval Observatory.
- p. United States Department of Agriculture.
- A. United States Department of Agriculture (Weather Bureau).

West Point (N.Y.)

- AB. United States Military Academy.

PHILOSOPHICAL TRANSACTIONS.

I. *An Experimental Investigation of the Thermodynamical Properties of Superheated Steam.—On the Cooling of Saturated Steam by Free Expansion.*

By JOHN H. GRINDLEY, B.Sc., Wh.Sc. Exhibition (1851) Scholar, late Fellow of the Victoria University.

Communicated by Professor OSBORNE REYNOLDS, F.R.S.

Received April 21, 1899—Read January 18, 1900.

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SECTION I.—*Introduction.*

In a paper on the "Dryness of Saturated Steam and the Condition of Steam Gas," read before the Manchester Literary and Philosophical Society on November 3, 1896, by Professor OSBORNE REYNOLDS, F.R.S., the following passage occurs, "The whole

theory of the properties of steam, as at present accepted, and all the steam tables are founded on the experiments of REGNAULT on the total heat of evaporation, so that if any other definition is given of saturated steam than that which results from boiling the water under constant pressure after it has been drained of entangled water by gravitation, these properties and tables will not apply." In the same paper Professor REYNOLDS describes a method of experimenting in which it is sought to determine whether, by sufficient wiredrawing of saturated steam at a known initial pressure and temperature, the steam could be finally brought into the condition of steam gas.

Having undertaken the experimental verification of the conclusions given in Professor REYNOLDS's paper, the author begs to point out the significance of the above extract in relation to any work which may be done in this subject, and to remark that it governs the methods and principles which have been adopted in the research, the results of which it is the object of this paper to describe.

The method given by Professor REYNOLDS is briefly as follows. If saturated steam be wiredrawn by passage through a small orifice from one chamber in which the pressure can be kept constant to another in which the pressure can be adjusted to have any lower value required, the steam in the second chamber will become superheated, and at first the temperature will fall, but if the pressure can be so far reduced in the second chamber that the amount of superheat contained by the steam is sufficient to render it perfectly gaseous, the temperature will be then unaffected by any further reduction in the pressure in the second chamber. Whether this "perfect gas" condition can be reached, by wiredrawing saturated steam from pressures up to 200 lbs. per square inch, is the question which it is the primary object of the present research to decide.

Before proceeding, however, very closely into the research, an examination of the theory of such wiredrawing experiments will reveal a point which would require definite settlement before the method described above could be adopted. In reducing the results of any wiredrawing experiments it would be necessary to know, or to possess some knowledge of, the precise law of flow which the steam obeys during its passage through the orifice. The usual theory adopted assumes that this law is the adiabatic one for saturated steam, but whether adiabatic flow is ever obtained in actual wiredrawing experiments is as yet undecided, and will, as mentioned above, require definite settlement.

Hence the author was recommended by Professor REYNOLDS to preface the research by an independent investigation into the laws governing the flow of steam through orifices of different natures. If it could be shown that the law of flow was never truly adiabatic, then the results of any wiredrawing experiments would not be capable of easy or accurate reduction to yield the thermodynamical properties which superheated steam possesses, but if such flow could be shown under certain circumstances to be adiabatic, then under these conditions the reductions would be both easy and direct.

The results of this preliminary inquiry, which are described in a paper* ("On the Law of Flow of Saturated Steam through Small Orifices"), recently presented to the Royal Society by the author, show clearly that adiabatic flow of saturated steam through an orifice occurs when the orifice is drilled in a piece of plate glass, under which circumstances the theory of the subject can be easily and directly applied to the experimental results.

Since the research is directly based on the experimental results of REGNAULT, it is necessary to at once accept as a definition of dry saturated steam that condition of steam which is obtained by draining from wet steam any entangled moisture, though it must be understood that as yet this condition has not been shown to be unique for any particular temperature and pressure of saturation, a point which can only be settled by experiment.

SECTION II.—*Short Theory.*

The account of the theory here given is that given by Professor REYNOLDS in the paper above quoted. Let p_1 be the pressure, T_1 the temperature, u_1 the velocity, and S_1 the dryness fraction of the steam before passing the orifice, and let the same letters with suffix 2 denote corresponding quantities after passing the orifice. Also let H_1 be the mechanical equivalent of the total heat of evaporation at pressure p_1 , and $H_1 - h_1$, the equivalent of the latent heat at the same pressure per lb. of dry saturated steam as determined from REGNAULT's steam tables. Let H_2 and $H_2 - h_2$ be corresponding quantities at the pressure p_2 , and let H_J denote the equivalent of any heat received from external sources. Let T_2 be the temperature of saturated steam at the pressure p_2 , a quantity to be determined from tables.

The total energy per lb. of fluid before passing the orifice is therefore

$$S_1(H_1 - h_1) + h_1 + \frac{u_1^2}{2g} + H_J,$$

and after passing the orifice the same quantity is

$$S_2(H_2 - h_2) + h_2 + \frac{u_2^2}{2g} + K(T_2 - T_1),$$

where K is the mean specific heat at constant pressure between the temperatures T_2 and T_1 . Since the energy of motion developed in the orifice is entirely returned as heat, by the law of conservation of energy we may equate the two quantities here found, and we get

$$S_1(H_1 - h_1) + h_1 + \frac{u_1^2}{2g} + H_J = S_2(H_2 - h_2) + h_2 + \frac{u_2^2}{2g} + K(T_2 - T_1) \quad (1).$$

Now in this equation if S_2 is not equal to unity we must have $T_2 = T_1$, and in this case we should have

$$S_1(H_1 - h_1) + h_1 + \frac{u_1^2}{2g} + H_J = S_2(H_2 - h_2) + h_2 + \frac{u_2^2}{2g} \quad (2),$$

* Not printed, but preserved for reference in the archives of the Society.

or, if S_2 is equal to unity, in which case the steam becomes superheated, we have

$$S_1(H_1 - h_1) + h_1 + \frac{u_1^2}{2g} + H_J = H_2 + \frac{u_2^2}{2g} + K(T_2^1 - T_2) \quad (3).$$

Further, if we make u_1 and u_2 small enough to be neglected, and ensure that $H_J = 0$, we get instead of (2) and (3) the equations

$$S_1(H_1 - h_1) + h_1 = S_2(H_2 - h_2) + h_2 \quad (4),$$

when S_2 is not equal to unity, and

$$S_1(H_1 - h_1) + h_1 = H_2 + K(T_2^1 - T_2) \quad (5),$$

when S_2 is equal to unity.

The second of these two equations is the one used in wiredrawing experiments in which it is sought to determine the initial dryness of the steam, for this purpose a value of K being assumed, which is usually REGNAULT'S determination of the mean specific heat at constant pressure (atmospheric) from 248° to 428° F. approximately.

Now from previous experiments made with superheated steam there appears to be good reason for thinking that when the steam is superheated to a considerable degree its condition approximates to that of a perfect gas. If in any wiredrawing experiments, such as those here described, the amount of superheating in the wiredrawn steam is sufficient to bring it to the gaseous condition, the temperature of the wiredrawn steam will suffer no further diminution, however much the wiredrawing be increased by lowering the pressure below the orifice. If such a condition could be experimentally obtained, it would be then easily possible to obtain the value K_p of the specific heat at constant pressure of steam gas. But RANKINE has proved* that if H_2^1 be the total heat of gasification of steam gas at temperature T_2^1 from any temperature T_0 at which saturated steam is sensibly a perfect gas, the operation being performed under constant pressure, then

$$H_2^1 = H_0 + K_p(T_2^1 - T_0) \quad (6),$$

where H_0 is the latent heat of evaporation of saturated steam at the temperature T_0 .

RANKINE assumed that saturated steam at 32° F. was sensibly a perfect gas, in which case the formula takes the form

$$H_2^1 = 1091.7 + K_p(T_2^1 - 32) \quad (7).$$

The formula may, however, be put in the more general form

$$H_2^1 = A + BT_2^1 \quad (8),$$

the constants A and B being obtained from any two experiments in each of which the perfectly gaseous condition is obtained by wiredrawing steam having a known total heat H_2^1 in its initial saturated condition.

* 'The Steam Engine,' p. 330,

SECTION III.—*Preliminary Experiments.*

After completing the experiments on the quantities of steam discharged from an orifice, as described in the paper before referred to, at Professor REYNOLDS'S advice, I made some experiments on the temperatures of the wiredrawn steam, using for this purpose a thermo-electric junction inserted in the steam, and a second similar junction in the same circuit immersed in an oil bath, the temperature in which (given by a thermometer) may be adjusted to have any required value, both junctions being in circuit with a galvanometer. The remainder of the apparatus was unaltered. When both junctions are at the same temperature no deflection of the galvanometer needle will be observed, and hence the temperature in the oil could be adjusted to that in the steam.

The object of these experiments was to observe to what extent the results would be affected by radiation.

The results obtained were very useful in this direction. The amount of lagging of the channel containing the wiredrawn steam was altered in different experiments made under the same initial conditions of pressure and temperature above the orifice, the comparison of the results showing that radiation affects the results to a very great degree, even with a fair amount of lagging.

The fall of temperature in the wiredrawn steam in any experiment was almost proportional to the difference of pressure, a result which is in accord with those of later experiments.

The results of these preliminary experiments showed clearly that before any accurate work could be done on the temperatures, the effect of radiation must be eliminated, and in the construction of the apparatus as finally used (see Section V.) the manner in which this was effected will be described.

SECTION IV.—*Nature of Orifice used.*

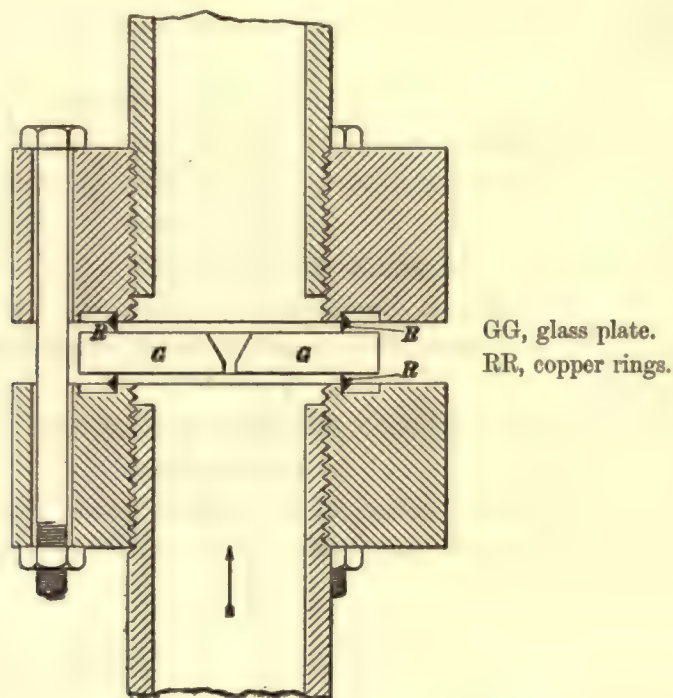
In the paper on the "Flow of Saturated Steam" it is shown that steam flowing through a circular orifice in a glass plate expanded according to the adiabatic law. As a glass plate would also diminish materially the passage of heat by conduction from one side to the other of the orifice, it has many advantages over other materials for wiredrawing experiments in which the difference of temperature on the two sides of the orifice may be considerable, sometimes amounting to 70° F. in the following experiments.

The orifice used was a circular one of about $\frac{1}{16}$ inch diameter drilled in a piece of plate glass $\frac{1}{4}$ inch thick. This orifice plate O, is fixed between two cast-iron flanges, F and F, figure 3, the joints being made by copper rings; the flanges are connected by three bolts $\frac{3}{16}$ inch in diameter, passing through holes in the flanges $\frac{1}{4}$ inch

diameter, thus preventing any material transfer of heat through the fastenings from the saturated steam to the wiredrawn steam.

The use of glass, however, increased the experimental difficulties considerably, for it often happened that the orifice plate would break during the heating of the apparatus, necessitating its removal and the insertion of a fresh plate before the experiment could be proceeded with. In the later experiments, made with great differences of pressure, the area exposed to this difference of pressure had to be reduced considerably for the plate to bear the combined differences of pressure and temperature. A full-size sectional view of the orifice plate and fastenings is shown in fig. 1.

Fig. 1.

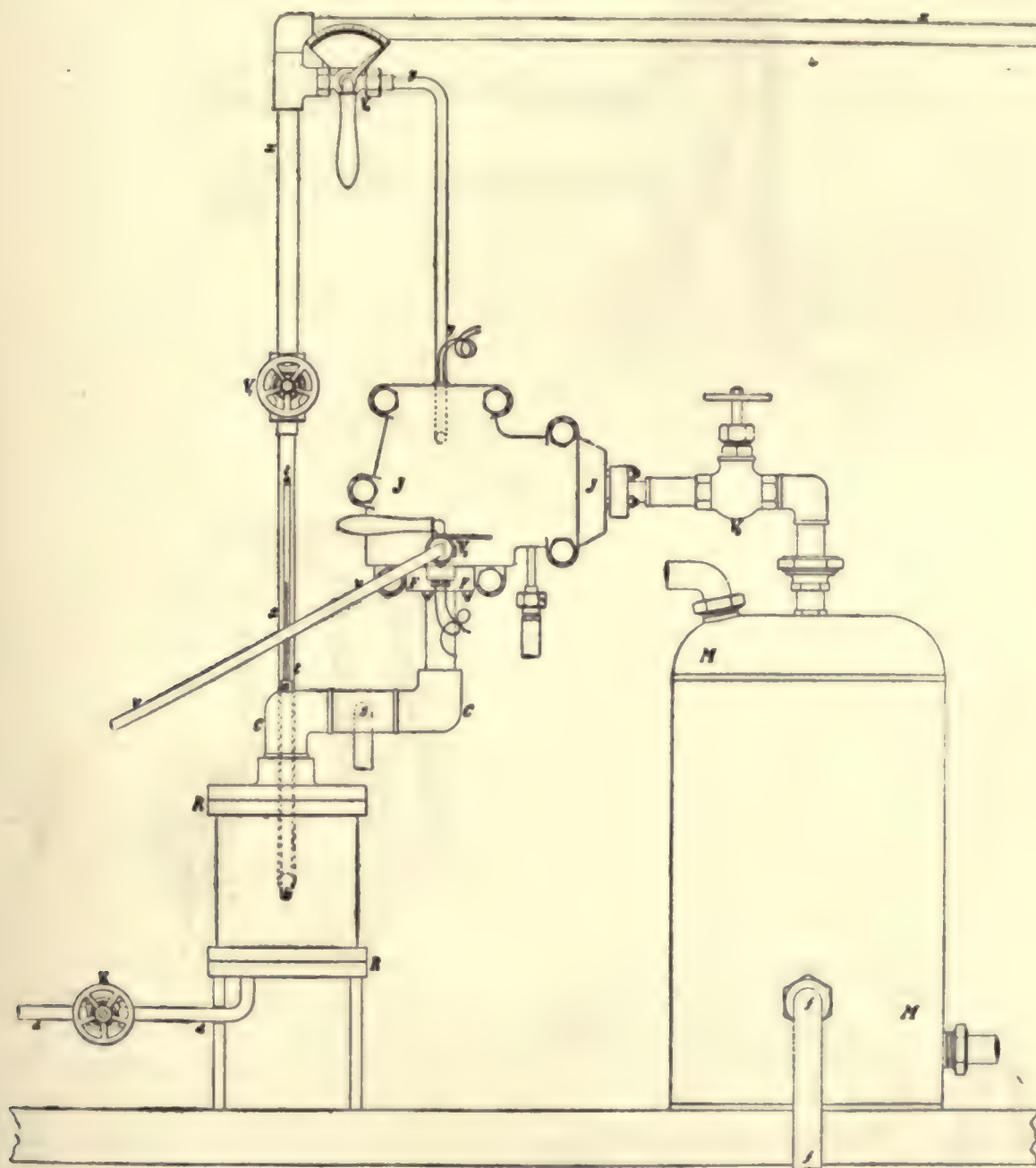


SECTION V.—*Description of Apparatus.*

A front view of the main portion of the apparatus is shown in fig. 2, RR being a vertical cylinder, forming a reservoir in which the steam is received through the pipe *xx* from the boiler. This reservoir or steam chest is of about 86 cubic inches capacity, and is provided with a drain pipe *dd*; the steam enters about the middle of its length, and the temperature in the chest is observed on a thermometer *tt*, standing in a tube *aa*, containing oil. The steam from this chamber flows upwards through the channel CC, leading from the centre of the upper cover to the orifice, the

plate containing which is just hidden by the steam jacket JJ, to be presently described. The portion of the channel enclosed by the steam jacket is shown in section in fig. 3, O being the orifice plate. The steam after passing the orifice

Fig. 2.



proceeds to the condenser MM, in fig. 3, and from thence by the pipe *ff* to an air vessel connected to an air pump (neither of which are shown in the figure).

The pressure in the chest RR is regulated by the valves V_1 in the admission

Fig. 3.

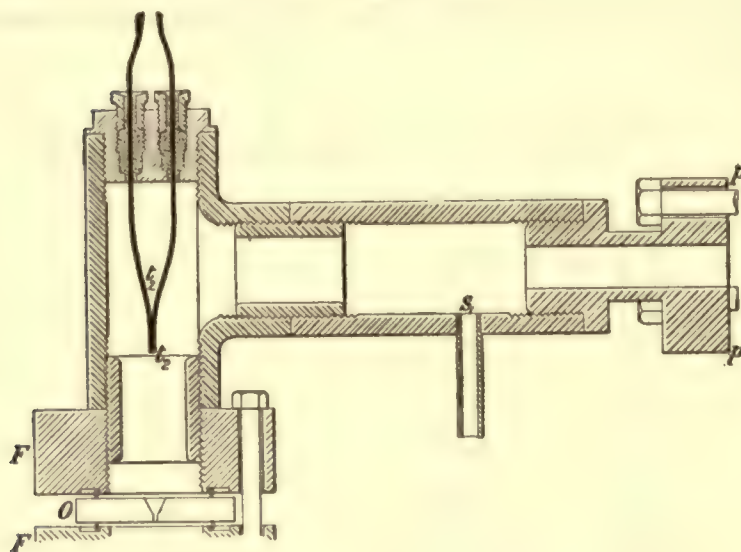
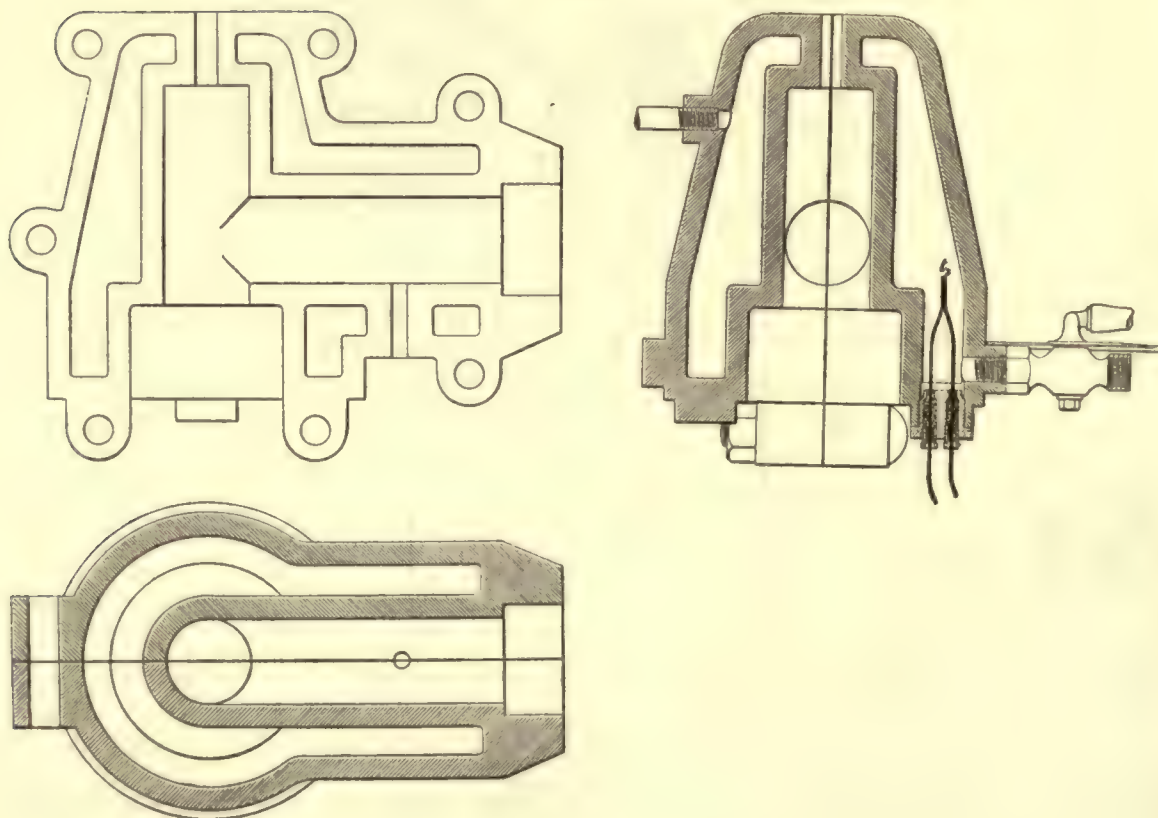


Fig. 4.



pipe and V_2 in the drain pipe, and its value is read by means of a pressure gauge, the siphon from which enters the channel CC at S. The pressure p_2 in the steam after passing the orifice is regulated by the valve V_3 ; but as the pressure below this valve is the same as that in the air vessel below the condenser, by sufficiently reducing this pressure in the air vessel by means of the air pump, it is possible to maintain any value of p_2 , ranging from 2 or 3 lbs. absolute to p_1 , the pressure in the chest RR.

The steam jacket to cover the channel containing the wiredrawn steam is shown in fig. 4. It was constructed so as to completely surround the channel leading from the orifice to a distance of about 8 inches from the orifice.

The portion of the channel surrounded by the jacket is separated from the other parts of the channel by the orifice plate O at one end, and by a ring of cork or asbestos at the other end pp , fig. 3. It consists of two sections at right angles to each other, a thermo-junction t_1t_2 entering at the elbow, and the siphon of a pressure gauge for registering the pressure p_2 entering at S_1 .

The steam jacket is supported by the channel it surrounds, and is itself a complete and enclosed vessel; it was made of cast iron, its thickness $\frac{3}{8}$ inch throughout, and was made in two halves, so that it could be removed, if required, without disturbing the remainder of the apparatus. These two halves are bolted together, the joints being made by rings of copper. The jacket steam was drawn from the pipe xx (fig. 2) coming from the boiler, by the branch pipe yy , and a small flow of steam was kept up through the drain pipe vv from the jacket. The temperature in the jacket was regulated to any desired value by altering the pressure of the steam in the jacket by the valves V_4 and V_5 in the admission pipe yy and drain pipe vv respectively.

The idea of constructing a steam cosie,* which should be entirely independent of the steam channel it surrounds, was due to Professor REYNOLDS, and the author is indebted to Mr. FOSTER, the chief assistant in the laboratory, for valuable aid in its construction.

Such, then, is the apparatus as finally used in the experiments. Its arrangement was, however, not altogether a simple matter of preconceived design, but was the outcome of continued adaptability and enlargement to meet the necessities and difficulties as they arose.

The source of steam supply when initial pressures up to 50 lbs. per square inch were used was a large Lancashire boiler used for heating purposes. When higher initial pressures were required, the author obtained permission from Professor REYNOLDS to use the locomotive boiler used in connection with the experimental engines in the Whitworth Engineering Laboratory of the Owens College, Manchester, and the author must express his indebtedness to the assistant, Mr. J. HALL, for the excellent manner in which the boiler pressure was kept constant during the long experiments.

* Used by REGNAULT in his latent heat experiments.

SECTION VI.—*On the Methods of Determining the Pressures and Temperatures.*

Into the reservoir RR a tube of brass *aa*, closed at the bottom, penetrates, as shown in fig. 2. This tube contains oil, and in it a thermometer is placed; the length of this thermometer immersed in oil being a matter of importance, it was sought to keep the amount of oil in the tube as constant as possible during the experiments.

The pressure of the steam before entering the orifice was observed on a Bourdon pressure gauge, the siphon from which enters the steam channel at S, between the reservoir and the orifice.

The pressure of the wiredrawn steam was observed, during the experiments with steam from the Lancashire boiler, by a mercury pressure gauge, and afterwards by a second Bourdon pressure gauge, the siphon from which passed through the jacket surrounding the channel, and entered the channel at S_1 , fig. 3.

The temperature of the wiredrawn steam was determined by inserting a thermo-junction of iron and copper into the steam channel, as at t_2t_3 , fig. 3, the wires passed out of the channel through two small glands in a brass plug, the joints being made with asbestos, which also formed the insulator for the wires. A second similar thermo-junction in circuit with the first is placed in an oil bath, the temperature in which could be adjusted to any required degree, the oil being stirred by two screw blades, worked by a small water motor. In this bath a thermometer was fixed, and the equality of temperature between the junction in the oil and the junction in the steam was shown by a galvanometer with mirror and scale. The ends of the copper wires from the two junctions dipped into two small mercury cups, and the ends of two copper wires from the galvanometer were dipped into these cups, completing the circuit. If any difference of temperature existed between the junctions, the galvanometer needle would be deflected, and by diminishing these deflections by altering the temperature of the oil bath, the final equality of temperatures between the thermo-junctions in the steam and oil was determined.

The difference of temperature between the steam in the jacket and the wiredrawn steam was observed by having a thermo-junction similar to that in the wiredrawn steam placed in the steam jacket at t_3 , fig. 4; a second similar junction was placed in the oil bath mentioned above.

These two junctions could now be brought into circuit with the galvanometer in a precisely similar manner to the other pair of junctions in the oil bath and the wiredrawn steam, as described already. When the oil bath temperature has been adjusted to equality with that of the wiredrawn steam, the galvanometer was immediately brought into circuit with the junctions in the oil and the steam jacket; any deflection of the galvanometer needle would now be proportional to the difference of temperature between the oil and the steam in the jacket, and therefore to the difference in the temperatures of the wiredrawn steam and the steam in the jacket.

The use of thermo-electric junctions to determine the temperature of the wire-

drawn steam was suggested to the author by Professor REYNOLDS. The direct determination of the temperature by the insertion of the thermometer in the steam would have increased the difficulty of obtaining correct temperature readings considerably, on account of the many corrections necessary.

SECTION VII.—*Method of Experiment.*

It was found necessary in beginning an experiment to warm the apparatus gently, as the orifice plate frequently cracked with sudden heating. When sufficient steam was passing through the apparatus and the required pressures attained, the admission valve was fixed sufficiently wide open to allow the maximum quantity of steam per minute required during the experiment to flow through it, and at the same time allow a sufficiency for drainage.

The pressure in the steam reservoir was then kept constant during the experiment by opening or closing the valve in the drain pipe according to the quantity required through the orifice. The opening in the valve V_3 beyond the orifice was then fixed so as to give any desired constant pressure to the wiredrawn steam; the temperature of the oil bath was then raised to equality with that of the wiredrawn steam, and the temperature in the steam jacket adjusted to equality with that in the oil bath by a few observations with the galvanometer. It was then necessary to wait for about 2 hours before a steady condition could be obtained; during this period the temperature of the wiredrawn steam would rise slowly, causing the temperatures in the oil bath and in the steam jacket to be continually readjusted.

After about 3 hours from the commencement of the experiment, the temperatures became sufficiently steady to allow readings to be taken. Observations of the temperatures in the steam reservoir and in the oil bath, and of the pressure below the orifice, are then taken as often as possible, intervals of 2 to 5 minutes elapsing between successive readings, the mean of successive readings taken over a period of from 15 to 30 minutes being taken as the correct reading, as shown in Table I.

The method of taking a reading is as follows:—The pressure being steady on either side of the orifice, the oil in the bath, which is kept at a slightly different temperature from that of the steam, is heated or cooled slowly, as required, during which period the galvanometer is brought several times into circuit with the junction in the steam, until the deflection of the needle ultimately vanishes. When this point is reached the temperature is noted on the oil bath thermometer; immediately this is read the galvanometer is brought into circuit with the junction in the steam jacket, and any deflection of the needle noted. These are entered along with the temperature in the reservoir and the pressure below the orifice in the following table, the column headed R—S giving the reading R before circuiting, and S the deflected reading; if R—S is positive, the steam in the jacket is hotter than the wiredrawn steam, and *vice versa*.

TABLE I.—Experiment 19.

Thursday, April 21st, 1898.

Boiler pressure about 33 lbs. by gauge.

Pressure in steam chest about 23·4 lbs. by gauge.

Time.	Temp. in Oil T_2	Pres- sure p_2	Mean T_2	Mean p_2	Initial Temp. T_1	R—S	Remarks.
10.15 a.m. 10.40 " 10.53 " 11.0 "							Pressure in steam chest 20 lbs. Bad leak. Steam shut off and orifice plate moved. Pressure in steam chest 22 lbs. Steady pressures.
1.33 p.m. 41 " 47 " 52 " 54½ " 57 " 59½ " 2.3 " 5½ " 8½ " 12 " 15 "	248·2 248·8 249·0 249·7 249·9 249·8 249·9 249·9 249·8 249·8 249·8 249·8	8·5 8·4 8·5 8·3 8·3 8·3 8·2 8·2 8·2 8·2 8·2 8·2	249·83	8·21	263·5 263·5 263·6 263·4 263·5 263·5 263·5 263·5 263·5 263·6 263·5 263·5	6·8 7·0 6·2 6·0 6·2 6·3 6·0 6·1 6·0 6·0 6·0 6·0 5·9 5·9 5·9 6·0 5·8 5·8 5·8 5·8 5·8 5·8 5·9 5·9	Boiler pressure 33 lbs. by gauge.
16 p.m. 28 " 32 " 41 " 45 " 47½ " 50 " 52½ " 55 "	254·2 254·2 254·4 254·4 254·4 254·4 254·4 254·4	17·0 17·0 17·1 17·1 17·1 17·0 17·0 17·0	254·4	17·05	263·5 263·5 263·6 263·5 263·5 263·7 263·5 263·5	5·8 5·7 5·9 5·8 5·8 5·7 5·8 5·8 5·7 5·7 5·7 5·6 5·6 5·6 5·6 5·6	p_2 altered. Boiler pressure 33 lbs.
56 p.m. 3.22 " 25½ " 29 " 32 " 35 " 38 " 40½ " 43 " 45½ " 47½ " 50 " 53 "	247·0 247·0 246·8 246·5 246·4 246·1 246·1 246·1 246·1 246·2 246·2 246·1 246·1	1·8 1·7 1·7 1·7 1·7 1·6 1·7 1·7 1·7 1·6 1·6 1·6 1·6	246·13	1·64	263·5 263·5 263·5 263·5 263·6 263·5 263·4 263·5 263·5 263·6 263·6 263·6 263·5	6·0 6·0 6·0 6·0 5·8 6·0 5·8 5·7 5·8 5·7 5·8 5·7 5·5 5·4 5·4 5·3 5·4 5·4 5·2 5·2 5·4 5·4 5·3 5·3	

Barometric height.	Time.	Temperature of air.
30·164	1·58	62·0°
30·160	2·53	62·5
30·153	3·51	62·5

TABLE II.

Boiler pressure.	Atmo-spheric pressure.	Pressure in chest.	T ₁ .	p ₂ (by gauge).	T ₂ .	Corrections for			Corrected values of		
						T ₁ .	p ₂ .	T ₂ .	T ₁ .	p ₂ .	T ₂ .
33 lbs. by gauges	14·84	23·4 by gauge.	263·5	8·21	249·83	- 2·0	- 1·55	0·7	Mean 361·5	21·5	250·5
			263·55	17·05	254·4		- 1·6	0·6		30·3	255·0
			263·5	1·64	246·13		- 1·2	0·7		15·3	246·8

In the lower of these tables is given the corrections and the corrected values of the mean temperatures and pressures drawn from the fourth and fifth columns in the first table.

An experiment usually lasts from 6 to 8 hours, during which time three to six mean values of T_2 for different values of p_2 will be found for any initial pressure and temperature in the reservoir.

SECTION VIII.—*The Correction of the Pressure Gauges.*

The Bourdon pressure gauges used during the experiments were corrected by means of a Bailey pressure gauge testing machine. In this machine the gauge is subjected to hydraulic pressure, obtained by placing as many weights as required upon a ram. The machine itself was subjected to examination by checking all the weights used, and also the sectional area of the ram; in this way the pressure per square inch produced by placing any weight upon the ram could be directly calculated. A further test was also made for small loads by the use of a mercury column to balance the pressure produced by the dead load on the ram.

The pressure gauges when tested showed the usual discrepancies of such gauges, but in tests made at various times during the research, the amount of the corrections was very closely determined. Especially was this the case with the pressure gauge used above the orifice, as it was by this gauge that the thermometers were corrected, and it is improbable that the error in the gauge when finally corrected could exceed 0·1 lb. per square inch in any part of the scale.

SECTION IX.—*The Correction of the Thermometers.*

Before proceeding to describe the method of correcting the thermometers used, it is necessary to repeat, as stated in the first part of this paper, that the research is based on REGNAULT's determinations of the relations between the pressure, temperature, and total heat of evaporation of saturated steam, and hence the definition of temperature assumed for the purposes of this paper is that saturated steam under a certain pressure has a fixed temperature given by REGNAULT's tabulated results.

The method of correction to be described was adopted since it removed the necessity of correcting the thermometers for the length of stems in the oil, and also any error which may arise from any of the junctions not finally attaining the same temperature of the steam or oil in which they are immersed. This method was to correct the thermometers in position in the apparatus, using the thermo-junctions, and without making any alterations except to substitute for the orifice plate another plate containing a large hole, which would not in any degree wiredraw the steam, so that saturated steam at a known pressure would occupy the whole of the channel and the steam chest; the outflow of steam, or the velocity of steam through the apparatus, could then be regulated by the valve on the low pressure side of the orifice. The pressure gauge relied upon to denote the pressure in the steam was the one used to give the pressure in the reservoir, its readings having been corrected as already described.

The operation of correcting the thermometers was then proceeded with as in an ordinary experiment, the only difference being that now the steam is always saturated in the apparatus.

Experiments were conducted on six days with this object, and from the results of these experiments the necessary corrections for both thermometers were obtained throughout the range of temperature required.

Hence it will be seen that the thermometers were used merely as instruments to effect a comparison of two temperatures, one of which was the temperature of saturated steam under a known pressure, and the other the temperature in the wiredrawn steam, so that the basis of the whole method has been reduced to a comparison between the temperatures of the wiredrawn steam and of saturated steam under known pressures when flowing with approximately the same velocity through the same portions of the apparatus.

SECTION X.—*Results of Experiments.*

The experiments on this subject were commenced in January, 1897, the earlier ones being chiefly devoted to determining the precautions necessary, and the best form of apparatus to use (see Section II.). These experiments showed that the chief source

of error was the radiation of heat from the channel containing the wiredrawn steam, this being remedied by the construction of a steam jacket.

The apparatus as finally used, and as described in Section IV., was ready for experiments in November, 1897, and as often as circumstances permitted experiments were made until July, 1898. The first experiments made, however, gave results of very little value, since it was proved that sufficient time had not been allowed for the steady condition of pressure and temperature to become established before taking observations, and henceforward particular attention was given during any experiment to obtaining a few temperature results at pressures covering a wide range of pressure ratio.

Among the many sources of experimental error encountered was one which for some time affected to a great extent the observations taken at very low pressures below the orifice, and which caused a great deal of trouble during the experiments. Thus, when observations at low pressures were being taken and continual pumping required to maintain those pressures, the temperature of the superheated steam could not be obtained with any degree of consistency.

The cause of this inconsistency appeared to be connected with the amount of pumping necessary, and in later experiments, where the low pressures could be maintained with little or no pumping for about half an hour, it was found that consistent readings could be obtained, and only readings obtained under these conditions are accepted and find place in the table of results given below.

The corrected results of twenty-eight experiments made with saturated steam at temperatures varying from 240° to 380° F. are given in the accompanying Table III., T_1 and p_1 being the initial temperature and pressure respectively of the saturated steam before wiredrawing, p_1 being taken from REGNAULT's steam tables, and T_2 the temperature of the wiredrawn steam corresponding to the pressure p_2 .

TABLE III.

No. of experiment.	p_1 .	T_1 .	p_2 .	T_2 .	Total heat of the steam from 32° F. in B.T.U.s.
1	24.9	239.8	16.5	232.35	1155.08
			8.9	226.4	
			5.05	224.4	
			8.9	226.75	
			18.1	232.65	
2	24.9	239.8	15.3	232.05	1155.08
			4.2	224.4	
			9.8	227.65	
			4.2	224.2	
			19.5	234.15	
3	24.9	239.8	19.3	234.55	1155.08
			4.6	224.2	
			18.6	233.25	

TABLE III. (continued).

No. of experiment.	p_1 .	T_1 .	p_2 .	T_2 .	Total heat of the steam from 32° F. in B.T.U.s.
4	52.5	284.0	27.9 15.6 3.4	268.7 261.5 254.35	1168.56
5	52.5	284.0	21.5 33.8 7.8 17.9	264.5 271.45 256.45 262.75	1168.56
6	52.5	284.0	17.2 36.6 5.05	262.4 272.9 256.1	1168.56
7	52.5	284.0	36.45 22.0 7.5	272.15 264.7 256.2	1168.56
8	36.8	262.0	18.1 34.1 6.4 25.3	248.9 256.75 240.8 252.3	1161.85
9	36.8	262.0	28.65 34.0 5.6 10.2	254.65 257.6 240.7 243.85	1161.85
10	66.2	298.9	54.8 19.95 28.5	290.1 272.15 277.2	1173.1
11	66.2	298.9	27.05 45.5 56.3 33.8 15.85 6.9	276.05 285.2 291.4 279.5 270.4 265.2	1173.1
12	66.2	298.9	18.2 38.6 6.9 7.1 4.5	271.95 282.15 265.3 265.5 264.5	1173.1
13	66.2	298.9	24.45 41.05 49.55 31.1 15.65	274.35 283.35 287.45 277.9 269.8	1173.1
14	66.2	298.9	15.2 49.65 58.3 15.85	270.2 287.4 291.05 270.5	1173.1

TABLE III. (continued).

No. of experiment.	p_1 .	T_1 .	p_2 .	T_2 .	Total heat of the steam from 32° F. in B.T.U.s.
15	126.55	345.05	32.7 63.7 91.1 71.35	302.9 316.3 328.1 319.05	1187.18
16	126.7	345.15	48.15 81.1 23.2 15.15	309.15 323.85 298.9 295.1	1187.21
17	126.85	345.25	69.8 96.8 32.2 17.2	319.2 329.6 303.1 296.3	1187.24
18	66.1	298.8	22.15	274.05	1173.07
19	36.7	261.5	21.5 30.3 15.3	250.5 255.0 246.8	1161.7
20	36.7	261.5	20.7	250.2	1161.7
21	36.7	261.5	25.75 33.15 30.05 15.8 6.9	252.5 256.6 254.25 246.2 241.7	1161.7
22	24.8	239.2	16.2 18.4 20.45 21.9 3.9	232.2 233.25 234.45 235.25 224.6	1154.9
23	24.8	239.2	16.4 7.6 4.6 2.45	232.15 226.2 223.3 222.4	1154.9
24	24.8	239.2	17.95 3.35	232.9 223.6	1154.9
25	195.25	379.55	71.95 111.5 151.4	337.05 350.85 363.3	1197.7
26	195.3	379.55	91.5 131.75 182.2	344.05 357.03 373.9	1197.7
27	195.3	379.55	111.65 48.2	350.75 326.9	1197.7
28	195.15	379.5	71.8 52.15 30.4 14.95	337.0 328.2 318.3 311.6	1197.69

SECTION XI.—*On the Effect of Altering the Condition of the Steam below the Orifice.*

The preliminary experiments and those numbered 1 to 10 in Table III. were made with steam from a Lancashire boiler. The steam was withdrawn upwards from this boiler through a channel consisting of $\frac{3}{8}$ -inch unlagged steam piping, which passed 2.5 feet vertically, then 64 feet horizontally, and finally 9.7 feet downwards to the steam chest. This great length of piping ensured a great amount of wetness in the steam when received in the steam chest. In the later experiments the steam was taken from a locomotive boiler much nearer the apparatus, the length of the connecting pipe ($\frac{3}{4}$ -inch steam piping) being 39 feet. In Experiments 19 to 24 this connecting pipe was well lagged with rough felting, as was also the steam chest; but, comparing the results of Experiments 19 to 21 with those of Experiments 8 and 9, which were made under the same initial conditions, or the results of Experiments 22 to 24 with those of Experiments 1, 2, and 3, it is shown very clearly that, though the condition of the steam in the steam chest when received from the boiler is very different in the two cases, no apparent difference is obtained in the condition of the wiredrawn steam.

The same point is also made clear by comparing the results of Experiments 15, 16, and 17. Experiment 15 was made with the channel from the boiler to the steam chest unlagged, the other two being made with the channel well lagged.

In Experiment 18, an attempt was made to alter, if possible, the initial dryness of the steam by working the injector for about 20 minutes during the experiment. This may have the effect of sending over more priming water by creating a stir in the boiler and also of introducing a little air into the boiler. A difference of 0.2° F. was all that was obtained, this being less than the error of experiment. The results of this Experiment 18, in which the steam pipe from the boiler and the steam chest were well lagged, show no apparent difference from those of Experiments 10—14, during which both the pipe and the steam chest were unlagged.

As a further experiment on the same point, the author tried to find in Experiment 20 the effect of altering the boiler pressure, the pressure in the steam chest being kept constant as usual. In this experiment, $p_1 = 23.4$ lbs. by gauge, or 36.7 lbs. per sq. inch absolute, and $p_2 = 20.7$ lbs. The boiler pressure during the first part of the experiment was 60 lbs. by gauge, and during the latter part 90 lbs., thus increasing the amount of wiredrawing between the boiler and the steam chest considerably. The mean temperature of the wiredrawn steam was found to be the same both before and after the alteration in the boiler pressure.

This experiment was then continued to observe what effect an alteration in the amount of drainage of steam over and above the water from the steam chest had upon the temperature readings. Keeping p_1 and p_2 the same as above, it was found that by almost closing the drain pipe valve so that only a very small quantity of steam

passed with the water from the steam chest, the temperature of the wiredrawn steam became lower by nearly 0.35° in about 10 minutes, and remained at this lower value so long as the drainage was thus restricted. This decrease of temperature was clearly noticeable, and, though its amount was relatively small compared with the increase of wetness in the steam in the steam chest, its existence seemed to impair in a slight degree the deduction that the condition of the steam was always the same just before entering the orifice.

There is, however, one point to notice which has not previously been mentioned, and which was suggested to the author by Professor REYNOLDS as accounting for this peculiar difference observed in the temperature of the wiredrawn steam; the water in the boiler is certainly not free from air, and even a small quantity of air in the steam entering the steam pipe with the steam, owing to the fact that a large quantity of steam leaving the boiler is condensed in the pipe and steam chest, would, if the actual steam drained away is very small, represent a much greater percentage of air entering the orifice with the steam than in the steam leaving the boiler. With good drainage of steam and water from the steam chest, this percentage of air would be very much smaller and most of it would be carried away through the drain pipe on account of its slightly greater density.

In any case, however, this maximum difference of temperature in the wiredrawn steam is scarcely sufficient, considering the good drainage usually allowed from the steam chest in the experiments and the general accuracy to which the results attained, to justify the conclusion that the conditions of the steam just before passing the orifice was ever materially altered.

An examination of all the results of experiments with steam of different conditions of wetness in the steam chest certainly shows that by withdrawing steam upwards from a steam chest containing wet steam, and allowing the moisture to separate by gravitation, the steam can always be obtained in the same condition as to dryness, and it is to these results that the author looks for experimental justification for taking the total heat of the steam before entering the orifice, to be given by tables deduced from the results of REGNAULT's experiments on the total heat of evaporation of saturated steam.

SECTION XII.—*On the Energy of Motion of the Steam at places where the Temperatures and Pressures are observed.*

Among the many causes which influence the results of experiments on the wire-drawing of steam, the energy of motion of the fluid at the places at which the temperatures and pressures are taken is perhaps the chief. As will be seen in the figure, the thermo-junction by which the temperature of the wiredrawn steam is ascertained, is about 2 inches from the orifice in a narrow channel, and it is to these temperature readings that we must look for the maximum effect of this energy of

motion. In the experiments the quantities through the orifice were always relatively small—the orifice being a small one.

In the first place, before making this point the subject of direct experiment, we may remark that the maximum quantities of steam per minute in any two experiments under the same initial conditions were not the same on account of the gradual closing of the orifice by fine particles of dust.

Thus Experiment 18, made under the same initial conditions as regards pressure and temperature to Experiments 10—14, gave results which were not different from those of the latter experiments, though the quantity of steam, when a maximum, in Experiment 18 was only 1 lb. in 40 minutes, while in Experiments 10—14 the maximum quantity would sometimes reach 1 lb. in 8 minutes, which would occur when the orifice was clean as in Experiment 13.

Similar variations in quantity and, therefore, in the energy of motion of the steam occurred in other experiments under the same initial conditions in which, again, no difference could be detected.

The results obtained, therefore, would indicate that the effect of energy of motion on the readings taken was too small to be noticed. To put the matter to a more severe test, however, an orifice of more than three times the sectional area of the one previously used was employed to repeat experiments at low initial steam pressures.

In the first experiment made with this orifice, the quantity of steam through the apparatus was so great that drops of water were carried through the orifice, being the water from the steam condensed just before the orifice was reached. No definite results could, therefore, be obtained as the condition of the wiredrawn steam seldom left the saturated state. The maximum quantity of steam used in this experiment was 1 lb. in 2.1 minutes, the initial temperature being 303° F.

The initial pressure was therefore reduced in the next experiment made with the same orifice. The initial temperature was 262.5° , the quantity of steam used per minute being at least three times greater than that in Experiments 19—21, the initial temperature in these experiments being 261.5° . The experiment gave four temperature readings which, when plotted, showed a mean deviation from the curve drawn through the results of 19—21 of 1.2° F.; as, however, the initial temperature was 1° higher, the difference is not sufficient to show definitely any marked effect of increasing the energy of motion of the steam at least threefold.

As, however, the velocity of the steam was raised in these experiments up to the point at which bubbles of water were carried through the orifice, it is impossible to put a greater test on the apparatus to find the effect of the energy of motion of the fluid on the temperature and pressure readings.

The energy of motion of the steam, after wiredrawing, at the place where the thermo-junction is placed to register its temperature, can also be approximately calculated, and, for present purposes, it will be sufficient to take the actual reading in the experiments at which this energy of motion will probably be greatest. On

examination of the pressures and quantities of steam through the orifice per minute, it appears that the reading at the pressure 14.95 lbs. in Experiment 28 will most probably feel the effects of this energy of motion to the greatest extent.

Taking now the sectional area of the channel, using the maximum rate of discharge of the steam in this experiment (1 lb. in 4.8 minutes), and making an approximation to the density of steam at a pressure 14.95 lbs. per square inch and temperature 311.6° F., the velocity of the steam at the place where the thermo-junction is placed works out at 41.6 feet per second. The energy of motion per lb. of steam at that velocity is 54.1 work units or 0.07 B.T.U. Taking the specific heat of superheated steam as 0.5, the fall of temperature due to this energy of motion is 0.14° F., which is much less than the experimental error, and, as this will be probably the maximum fall, being very much less than this for by far the greater part of the readings taken, it will not be necessary to make any corrections upon this head.

The effect of the velocity of the steam on the observed pressure may also be approximately calculated; but, taking the maximum quantities, the loss of pressure due to this cause never exceeded 0.1 lb. on the sq. inch, and, as it is usually very much less than this, we need not take this loss into account.

SECTION XIII.—*On the Position of the Thermo-junction in the Steam.*

After Experiment 27 had been made, a second thermo-junction was inserted in the channel on the low pressure side of the orifice, the junction being placed in the horizontal portion of the channel, about $3\frac{1}{2}$ inches from the orifice. The wires from this junction passed out of the channel between the two flanges at the end *pp*, fig. 3, of that portion covered by the steam jacket. Another similar junction in the same circuit was placed in the oil bath, and the galvanometer was brought into the circuit by the same process as with the previous circuit, viz., by dipping the ends of the wires into mercury cups into which the ends of the wires from the galvanometer can be dipped. By this means either the old circuit or the new one can be brought into the galvanometer circuit. As the above alteration includes the making of an entirely new circuit, which is differently placed in the apparatus to the old one, small differences may exist between the readings given by the two circuits. Hence in any experiment made with the aid of the new circuit the thermometric observations should be corrected by again comparing the temperatures found with those of saturated steam under known pressures, using this same circuit to effect the comparison. An experiment was then made with the new circuit in position, with the object of ascertaining whether the superheated steam had different temperatures in different parts of the channel. The observations taken during this experiment showed a mean increase on those of previous experiments made under the same initial conditions of 1.2° F., the rate of fall of temperature with pressure in the wiredrawn steam being the same as that indicated in previous experiments.

This result appeared very interesting, and appeared to lead to something which may have affected the results considerably, all that is necessary to know now being that the comparison of temperatures given by this circuit is the same as that by the previous one.

To effect this comparison an experiment was made with saturated steam under known pressures flowing through the apparatus, the orifice plate having been removed for this purpose in precisely the same way as described in correcting the thermometers. When the conditions were steady, each of the two circuits from the junctions in the steam were brought in turn into circuit with the galvanometer. The mean of the actual readings on the thermometer in the oil bath given by the two circuits were 248.05° by the new circuit and 246.95° by the old one, and again 248.0° by the new circuit, the difference being about 1.1° F.

Thus it appears that when the results given by the new circuit are corrected in the same manner as were those with the previous circuit, the corrected results do not differ by an amount so great as the natural error of experiment, and above all it is shown that experiments made with the junction immersed in the steam in the horizontal portion of the channel, and therefore not in a position directly opposite the orifice, as is the case with the old junction, would give results which within the limits of experimental accuracy do not differ from those already obtained with the old circuit.

In the last experiment made (No. 28), since the temperatures were here very high, and the flow of steam very great, after the completion of the experiment with the aid of the old circuit, the new circuit was brought into play to see if this same difference existed at higher temperatures. The actual readings taken with the old circuit at the pressure 15.75 lbs. being 310.25° , and with the new circuit 311.3° , the difference being 1.05° , which is practically the same as that found to exist between the observations given by the two junctions at lower temperatures. Hence, as has been shown, the same results would have been obtained had either of the two positions in the steam channel been initially chosen to place the thermo-junction.

SECTION XIV.—*On the Transference of Heat across the Orifice Plate.*

In the experiments made with high initial temperatures the difference of temperature on the two sides of the orifice plate sometimes amounted to over 50° , and if only a small quantity of steam is flowing through the channel the heat transferred from one side to the other of the orifice may become relatively very important.

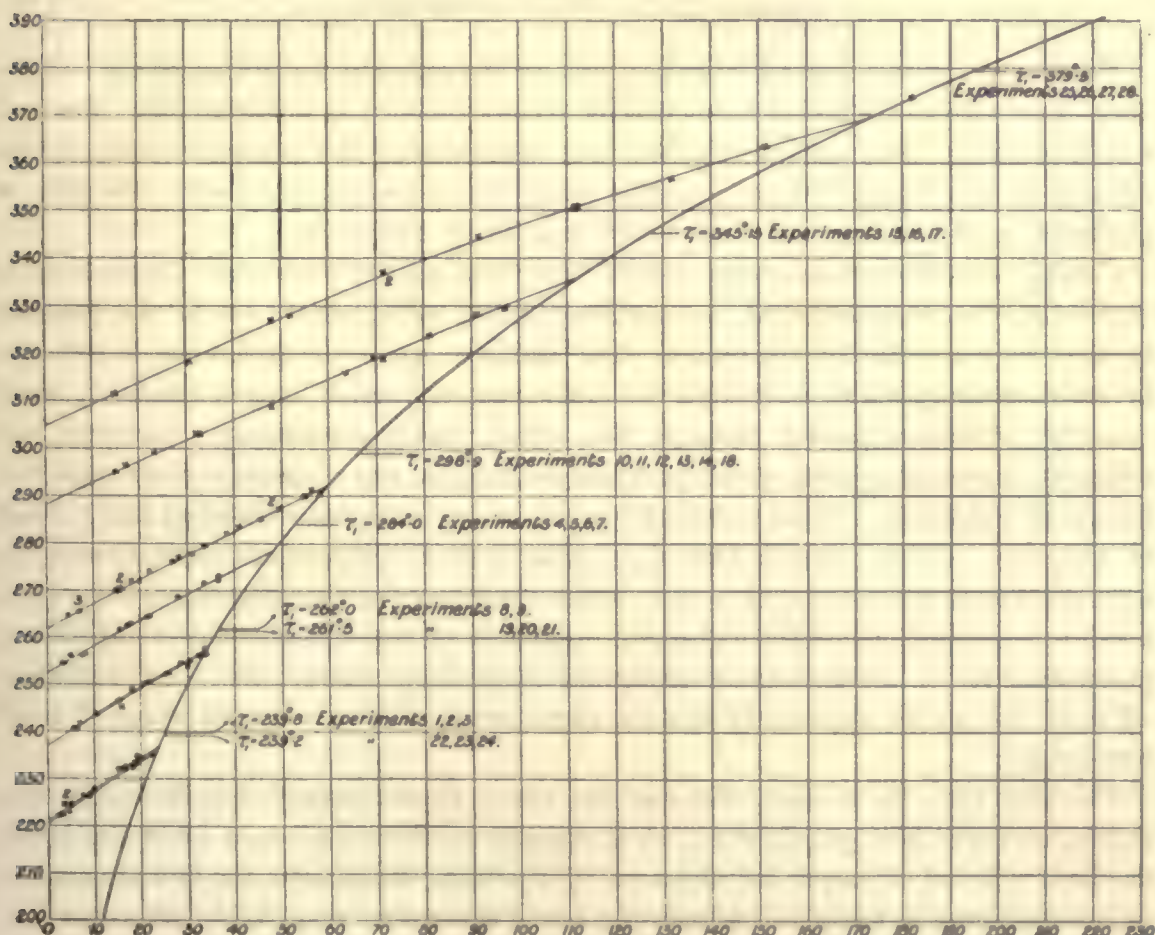
In order to calculate the maximum difference of temperature caused by this transference, the author took an hypothetical case in which the difference of temperature on the two sides of the orifice plate was 50° F., and the quantity of steam 1 lb. in 12 minutes, the effect of this combination of circumstances being greater than any actually experienced in the experiments. Thus the quantity of heat conducted

through a glass plate $\frac{1}{4}$ inch thick and of sectional area 1.11 sq. inches, with a difference of temperature of 50° F. on its faces, would be about 0.037 B.T.U. per minute, and taking the specific heat of the superheated steam as 0.5 and the quantity of steam 1 lb. in 12 minutes, the rise of temperature of the wiredrawn steam is calculated to be nearly 0.9° F. As in actual experiments the difference of temperature due to this transference of heat by conduction will be much less than this, no attempt has been made to correct the actual results for these differences.

SECTION XV.—*Reduction of the Observations.*

The performance of any of the experiments here described will give a series of relations between the pressure and temperature of the wiredrawn steam for a particular initial condition of the steam as regards its pressure and temperature. If now these results be plotted on a diagram with pressures for abscissæ and temperatures as ordinates, we get a series of points as shown in Diagram 5. On this diagram the initial condition of the steam in any experiment is shown on the

Diagram 5.



saturation curve, the number of the experiment being also indicated. When the experiment was made with steam from the large Lancashire boiler, the points representing the p — t relations observed are indicated by small circles.

Suppose now that through the points thus obtained a series of curves be drawn to represent the law of cooling from any initial condition. It will be found that if a mean curve be drawn through all the points obtained by using steam in a given initial condition, it will also be a mean curve for the points obtained from any single experiment at the same initial pressure and temperature. The relative accuracy which the experiments attain is clearly shown by the diagram, the greatest distance from any point representing the p — t relation in any experiment to the mean curve through the points obtained in all experiments under the same initial conditions being little, if any, greater than the expected error of experiment under that particular p — t relation.

The use of these curves will facilitate the deductions from the experiments of the actual law of cooling of the steam and of the variation of the specific heat at constant pressure with both pressure and temperature.

SECTION XVI.—*Summary of Results.*

The first point of importance brought out by the experiments is that so far as they have been carried the steam never became what is known as a perfect gas. For had such a condition been arrived at, the curve representing the pressure—temperature relation in the steam in that condition would have become parallel to the axis of pressures, as the cooling would then have practically vanished.

Coming now to consider any one of the mean curves drawn on Diagram 5, it may be at once remarked that the portions of the curve which are of the greatest interest were the hardest to obtain. For instance, when the difference in the two pressures causing the flow through the orifice was very small, only a relatively small quantity of steam passed through the orifice, which considerably increased the difficulty of obtaining accurate temperature readings in the wiredrawn steam near the saturated condition. Those results, however, which have been obtained and plotted in Diagram 5 show clearly that the actual fall of temperature with pressure is most accurately represented by a curve which commences at the point on the saturation curve representing the initial saturated condition of the steam before wiredrawing, proceeding for a short distance along the saturation curve, and then branching off from this at an apparently definite angle, proceeding in a regular curve of small curvature.

The fact that for a short distance the curve approximately coincides with the saturation curve is very important, as it appears to show that even after the steam has been relieved of suspended moisture by a process of drainage, the law of pressure and temperature in the steam follows the law of saturation very closely till saturation

is exhausted, when the steam suddenly follows the law of gases. It should be remembered, however, that in the actual experiments the wetness of the steam in the steam chest from which the steam supply is taken was altered as much as possible in different experiments under the same initial pressures and temperatures, but it was not found possible to affect the apparent dryness of the steam just before entering the orifice by an amount which came within the limits of observation, it being here noted that if the dryness fraction of the steam before entering the orifice had been altered by so little as 0.06 per cent. (the temperature of saturation being 284° F.), a difference of 1° F. would have been observed in the temperature of the wiredrawn steam, a quantity which would at once have been observed.

The experiments, therefore, indicate that even after relieving the steam of moisture by gravitation, there is still an effect as if a small quantity of moisture were present in the steam.

The curve representing the pressure temperature relation in the steam wiredrawn from a definite initial condition coincides for a short distance with the curve representing the law of saturation in Diagram 5, and the length of the coincident portions varies with the initial temperature of the steam, the approximate fall of temperature during the coincidence of the curves being represented by the following table :—

Initial temperature of saturation.	Fall of temperature before the gaseous condition is established.
239.2° F.	2.8° F.
239.8	2.8
261.5	4.7
262.0	4.7
284.0	5.5
298.9	6.6
345.15	9.15
379.5	10.5

Taking the first row in this table, it would appear that saturated steam wiredrawn down till it first becomes gaseous at 236.4° possesses a total heat of gasification under constant pressure identical with the total heat of evaporation of dry saturated steam at 239.2°, and, further, that dry saturated steam at 236.4° is not steam gas, but possesses what is equivalent to a dryness fraction of 99.91 per cent. In a similar manner dry saturated steam (as defined at the commencement of this paper) at 369° F. would apparently have a dryness fraction of 99.63 per cent. to bring it to steam gas.

Proceeding now to examine the lower ends of these curves of free expansion, it will be noticed that the curvature of the curves is very small and regular, even to pressures of 2.5 lbs. per square inch absolute. If now these curves be continued to the zero pressure line as curves of the same curvature throughout (which may or may

not represent the true law of cooling at pressures below those obtained in the experiments), the values of the specific heat at constant pressure deduced by taking the temperatures given by the intersection of these curves of free expansion with the zero pressure line show a continual increase with the temperature, which again requires careful consideration, for if steam at ordinary temperatures (under 400° F.) is ever sensibly a perfect gas, it will be so at very low pressures, and it has been assumed by RANKINE that at a pressure of 0.085 lb. per square inch and temperature 32° F. saturated steam is a perfect gas, but in a perfect gas the specific heat at constant pressure is independent of the temperature, so that if steam at very low pressures is a perfect gas, the values of the specific heat at constant pressure given by the various intersections of these curves of known constant total heats with the line of zero pressures should be the same for all temperatures. Hence, either the curves as drawn at pressures below those attained in the experiments are very far from representing the true law of cooling or steam even when indefinitely rarefied at ordinary temperatures is never even approximately a perfect gas.

The latter deduction would appear to be the most correct as no indication of any change in the curvature of the curves of free expansion is found even at low pressures of $2\frac{1}{2}$ lbs. per square inch, and the change of curvature would have to be very sudden and very great in order to create anything like a constant value of the specific heat at constant pressure, an examination of the sort of curve required showing such changes to be very unreasonable.

To find the variation in the value of the specific heat at constant pressure with temperature, the curves of free expansion on Diagram 5 are used, the intersections of the curves with any line of constant pressure giving a series of temperatures between each pair of which the mean specific heat of the steam may be found in the following manner. If H_1 be the total heat of evaporation of saturated steam which, when freely expanded to a pressure p , will be at a temperature T_1 , and H_2 the total heat of steam, which, when expanded freely to the same pressure p , will be at a temperature T_2 , the value of the specific heat at pressure p between temperatures T_1 and T_2 is

$$\frac{H_1 - H_2}{T_1 - T_2}$$

for, by equation 5, page 4, if we wiredraw dry steam ($S = 1$) from a saturated condition having a total heat of evaporation H_1 to a temperature T_1 and pressure p , at which the temperature of saturation is T_3 and total heat of evaporation H_3 , we have

$$H_1 = H_3 + K(T_1 - T_3).$$

Similarly by wiredrawing from a saturated condition represented by a total heat H_2 to a temperature T_2 at the same pressure p , we have

$$H_2 = H_3 + K(T_2 - T_3),$$

and hence by subtraction

$$K = \frac{H_1 - H_2}{T_1 - T_2},$$

K now being the mean specific heat at constant pressure between temperatures T_2 and T_1 .

This formula, which is easily applied to the experimental results just given, is, however, not quite so accurate as its deduction from the general theory would lead one to suppose, for it has been shown by HIRN that by neglecting to take account of the energy existing in the liquid water at the temperature from which the total heat of evaporation is measured, in this case 32° F., an error is introduced which may under certain conditions become appreciable, and hence the formula just quoted will be discarded in favour of the more complete expression given by HIRN in his 'Théorie Mécanique de la Chaleur' (Tome I., 3^{me} édition, Paris, 1875, p. 434), viz.

$$K_p = \frac{H_1 - H_2 + \frac{0.016}{774} (P_1 - P_2)}{T_1 - T_2},$$

where the 0.016 in the numerator is the volume in cubic feet of 1 lb. of liquid water, 0.774 being JOULE'S equivalent, P_1 and P_2 being the pressures from which the wire-drawing takes place, and the remainder, as in the previous formula, for K.

By the aid of this formula the values of the mean specific heat at constant pressure have been calculated for various pressures and between certain temperatures, the results being tabulated in the following Table IV.

TABLE IV.

Pressure, lbs. per sq. inch.	Temperatures between which the specific heat is taken.		Difference of temperature, $T_1 - T_2$.	$H_1 - H_2 + \frac{0.016}{774}(P_1 - P_2)$.	Mean specific heat.
5	224.1	240.3	16.2	6.8216	0.4211
	240.3	255.4	15.1	6.8331	0.4525
	255.4	264.6	9.2	4.5853	0.4984
10	227.5	243.5	16.0	6.8216	0.4263
	243.5	258.1	14.6	6.8331	0.4680
	258.1	267.2	9.1	4.5853	0.5039
14.7	230.7	246.5	15.8	6.8216	0.4317
	246.5	260.8	14.3	6.8331	0.4778
	260.8	269.7	8.9	4.5853	0.5152
	269.7	295.0	25.3	14.286	0.5646
	295.0	311.5	16.5	10.696	0.6482
20	234.3	249.5	15.2	6.8216	0.4488
	249.5	263.8	14.3	6.8331	0.4778
	263.8	272.5	8.7	4.5853	0.5270
	272.5	297.4	24.9	14.286	0.5737
	297.4	313.8	16.4	10.696	0.6522

TABLE IV. (continued).

Pressure, lbs. per sq. inch.	Temperatures between which the specific heat is taken.		Difference of temperature, $T_1 - T_2$.	$H_1 - H_2 + \frac{0.016}{774}(P_1 - P_2)$.	Mean specific heat.
25	252.3	266.6	14.3	6.8331	0.4778
	266.6	275.0	8.4	4.5853	0.5459
	275.0	299.6	24.6	14.286	0.5807
	299.6	316.2	16.6	10.696	0.6443
30	255.0	269.3	14.3	6.8331	0.4778
	269.3	277.6	8.3	4.5853	0.5524
	277.6	301.8	24.2	14.286	0.5903
	301.8	318.4	16.6	10.696	0.6443
35	271.9	280.1	8.2	4.5853	0.5592
	280.1	304.0	23.9	14.286	0.5977
	304.0	320.7	16.7	10.696	0.6405
40	274.4	282.6	8.2	4.5853	0.5592
	282.6	306.2	23.6	14.286	0.6053
	306.2	323.0	16.8	10.696	0.6367
45	277.0	385.1	8.1	4.5853	0.5661
	285.1	308.4	23.3	14.286	0.6131
	308.4	325.4	17.0	10.696	0.6292
50	287.6	310.5	22.9	14.286	0.6238
	310.5	327.5	17.0	10.696	0.6292
55	290.2	312.7	22.5	14.286	0.6349
	312.7	329.7	17.0	10.696	0.6292
60	314.8	331.8	17.0	10.696	0.6292
65	317.0	333.9	16.9	10.696	0.6329
70	319.0	335.9	16.9	10.696	0.6329
75	321.2	337.9	16.7	10.696	0.6405
80	323.3	339.7	16.4	10.696	0.6522
85	325.4	341.6	16.2	10.696	0.6602

That a large variation in the value of the specific heat takes place with temperature is clearly shown in the last column of this table; its variation with pressure is not, however, quite so evident. To enable a simple comparison to be made, certain figures are taken from the above table which show the values of the mean specific heats under different pressures but near the same temperature. These are placed in the following Table V., and the comparison this table affords shows very clearly that if there is any variation in the value of the specific heat at constant pressure with pressure it must be very small, especially when viewed in comparison with the variation with temperature as shown by the previous table.

TABLE V.

Temperatures between which mean specific heat is taken.		Mean temperature.	Pressure, lbs. per sq. inch.	Mean value of the specific heats.	
{	255.4	264.6	260.0	5	0.4984
	252.3	266.6	259.45	25	0.4778
{	258.1	267.2	262.65	10	0.5039
	255.0	269.3	262.15	30	0.4778
{	269.7	295.0	282.35	14.7	0.5646
	272.5	297.4	284.95	20	0.5737
{	277.0	285.1	281.05	45	0.5661
	295.0	311.5	303.25	14.7	0.6482
{	297.4	313.8	305.6	20	0.6522
	290.2	312.7	301.45	55	0.6349

Hence as regards the values of the specific heat under constant pressure of superheated steam the results of the experiments show that a very large variation in its value occurs with temperature, but its value is practically independent of the pressure.

We see therefore that since the "perfect gas" condition is never obtained in the steam in the experiments, it is impossible to calculate the constants in equation 8, p. 4, or to in any way use RANKINE'S formula 7 for the total heat of gasification of steam anywhere within the limits of pressure and temperature used in these experiments.

SECTION XVII.—*Added October 4, 1899.*

Comparison with previous experiments.

It has been suggested to the author that a comparison of the experimental results with those of previous experimenters would be of interest, and for the sake of comparison, HIRN'S experimental results have been taken, as no others have been made which enable even a small comparison to be made. It may be remarked, however, that experiments such as those by PARENTY,* or by PEABODY and KUHNHARDT,† though not undertaken with the same object as in the present ones, emphasise the difficulty of obtaining accurate results in this class of experiments. As regards the high values which have been obtained for the value of the specific heat under constant pressure in superheated steam in the present experiments, though in view of REGNAULT'S experimental result of 0.4805 for the mean specific heat between 248° F. and 430° F. they seem highly improbable, there is no direct evidence that a very large variation in its value does not occur, what evidence exists tending in fact to show that very large variations do actually occur; thus, DELAROCHE and BERARD‡ found that $K_p = 0.847$, while recently the value 0.38 has been calculated for the

* 'Ann. de Chimie et de Physique', 7me série, tome xii., 1897.

† 'Proceedings American Society of Mech. Engineers,' 1890.

‡ Vide ZUENER'S 'La Chaleur,' p. 422.

mean specific heat at atmospheric pressure between 212° and 260° F., the data for the calculations being obtained from REGNAULT's experimental results.* ZUENER† has also calculated the value $0.568 = K_p$ by assuming a certain law of expansion to hold in the superheated steam.

The experiments of HIRN, however, afford under atmospheric pressure only a direct comparison with those of the present research, as from the temperatures he obtained by wiredrawing saturated steam from certain initial pressures to atmospheric pressure it is possible to calculate by his formula quoted above the values of the specific heat at atmospheric pressure between certain temperatures. The results have been tabulated in Table VI., in which are also given the results of the present experiments. This table is certainly very interesting, as it shows most clearly that a larger variation exists in the value of K_p as deduced from HIRN's experiments than the variation deduced from the present experiments.

TABLE VI.—On the values of the Specific Heat K_p at atmospheric pressure as deduced from HIRN's experimental results and as calculated from the present experiments.

Results calculated from HIRN's experimental figures.

Temperatures between which the specific heat is taken.		Mean specific heat K_p .
239.0	263.12	0.3048
263.12	271.4	0.6742
271.4	279.9	0.5362
279.9	287.06	0.5428
287.06	291.38	0.7874
291.38	296.6	0.5839
296.6	301.23	0.5977
301.23	306.5	0.9258
306.5	312.04	0.8028
312.04	314.06	0.9577
314.06	316.04	0.9309

Present Experiments.

Temperatures between which the mean specific heat is taken.		Mean specific heat K_p .
230.7	246.5	0.4317
246.5	260.8	0.4778
260.8	269.7	0.5152
269.7	295.0	0.5646
295.0	311.5	0.6482

* MACFARLANE GRAY, 'Trans. Inst. Naval Arch.,' 1889.

† ZUENER'S 'La Chaleur,' p. 441.

As will be seen from the last column in this table, the values of K_p deduced from HIRN's experiments are very inconsistent with one another, a careful examination of them showing, however, that as a rule the variations of K_p shown by HIRN's results is greater than that deduced from the present experiments, and further that HIRN's results show a distinctly higher value for K_p under atmospheric pressure and about 300° F.

SECTION XVIII.—*Added October 4, 1899.*

On the Cooling Effects observed in the Wiredrawn Steam.

It will be seen on Diagram 5 that the fall of temperature along a line of free expansion is not exactly proportional to the difference of pressure, the lines of free expansion being slightly convex upwards.

Again, in the experiments of JOULE and THOMSON on the cooling effects observed by wiredrawing different gases through a porous plug, it was observed that the cooling effect was almost proportional to the inverse square of the absolute temperature. To observe how far this was true for steam, there were obtained from Diagram 5 various values of the cooling effect $\delta\theta/\delta p$, or, as we will in future call it, C, and by plotting the logarithms of these values of C and of the absolute temperatures T, it appeared that C varied approximately as $(1/T)^{3.8}$, the index 3.8 being very different to the value 2 obtained by JOULE and THOMSON.

SECTION XIX.—On certain *Thermodynamical Relations* existing between the Cooling Effect, the Specific Heat K_p , and Density of Superheated Wiredrawn Steam.

It early suggested itself to the author that some simple relation existed between the variations in the value of K_p with pressure and temperature, and an examination showed that the cooling effect $C(=\delta\theta/\delta p)$ was connected to K_p in the following relation

$$\frac{\partial}{\partial p}(\mathbf{K}_P) = - \frac{\partial}{\partial T}(\mathbf{CK}_P) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{a}),$$

showing that the variation in the value of K_p with the pressure is equal to, but of opposite sign, to the variation with temperature of the product of K_p with the cooling effect. This formula may be deduced in the following manner. From THOMSON'S formula* for the cooling effect produced by wiredrawing, we have

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{v + (K_p)}{T} \dots \dots \dots (\beta),$$

* TAIT'S 'Heat,' (1892), p. 340.

where T is the absolute temperature and v the specific volume of the wiredrawn gas or vapour, and by differentiation we obtain

$$\frac{d^2v}{dT^2} = \frac{1}{T} \frac{\partial}{\partial T} (CK_P) \quad (\gamma),$$

but by RANKINE'S* formula for the specific heat

$$K_P = \text{constant} - T \int_0^P \frac{d^2v}{dT^2} dp;$$

we obtain by differentiation

$$\left(\frac{\partial K_P}{\partial p} \right)_T = -T \frac{d^2v}{dT^2} \quad (\delta).$$

Hence by comparing γ and δ we have the relation (a). The simplest method of deducing the formula is by considering a small parallelogram on the $p-t$ diagram, bounded by lines of free expansion and lines of constant pressure.

We have therefore a very simple formula for checking the experimental results just obtained, for if K_P does not vary with the pressure as is indicated by Table V., then the product CK_P must be independent of the temperature at any particular pressure. In order to obtain the values of K_P at temperatures for which the cooling effect is shown on Diagram 5, constant pressure curves were drawn on a diagram having for abscissæ absolute temperatures and for ordinates the values $H_1 + \frac{0.016}{774} P_1$, as explained on p. 27, H_1 being the total heat of evaporation of the steam before wiredrawing from a pressure P_1 and 0.016 representing the specific volume of water at 32° F., the slopes of these curves giving the values of the specific heat under constant pressure at any particular temperature and for the particular pressure at which the curve is drawn. In this manner the results given in the Table VII. were obtained and the necessary calculations made.

From the fifth column of this table it will be seen that the product CK_P is practically independent of the temperature, and from the sixth column that it is also independent of the pressure, *i.e.*, CK_P is constant between pressures of from 10 to 50 lbs. per square inch, and between temperatures of 227.5° and 327.5° F.

The mean value of CK_P throughout this range of pressure and temperature is 0.2819. Outside this range of pressure it is impossible to give very accurate results, but as no great and distinct variations actually appear, it would seem that the constancy of CK_P could be accepted beyond this range of pressure and temperature.

The fact that the product CK_P is practically constant is of very great importance, as it will simplify many deductions from expressions in which CK_P only occurs as a product.

For example, formula B just quoted gives a relation between v , T , C , and K_P

* RANKINE'S 'Steam Engine,' p. 317.

TABLE VII.

Pressure, lbs. per sq. inch.	Temperature.	Cooling effect, C.	Specific heat, K_p .	Product, CK_p .	Mean product, CK_p .
10	227.5	0.690	0.400	0.2760	0.2789
	243.5	0.646	0.447	0.2888	
	258.1	0.568	0.488	0.2772	
	267.2	0.524	0.520	0.2725	
	292.8	0.460	0.609	0.2801	
14.7	230.7	0.664	0.404	0.2683	0.2838
	246.5	0.604	0.465	0.2809	
	260.8	0.570	0.512	0.2918	
	269.7	0.524	0.527	0.2761	
	295.0	0.456	0.613	0.2795	
	311.5	0.450	0.680	0.3060	
20	234.3	0.654	0.432	0.2825	0.2837
	249.5	0.582	0.477	0.2776	
	263.8	0.554	0.512	0.2836	
	272.5	0.516	0.541	0.2792	
	297.4	0.450	0.621	0.2794	
	313.8	0.450	0.666	0.2997	
30	255.0	0.550	0.479	0.2634	0.2787
	269.3	0.524	0.522	0.2735	
	277.6	0.508	0.555	0.2819	
	301.8	0.444	0.621	0.2757	
	318.4	0.450	0.664	0.2988	
40	274.4	0.508	0.551	0.2799	0.2832
	282.6	0.500	0.588	0.2940	
	306.2	0.440	0.621	0.2732	
	323.0	0.438	0.652	0.2856	
50	287.6	0.496	0.606	0.3006	0.2821
	310.5	0.432	0.623	0.2691	
	327.5	0.430	0.650	0.2795	

which, since CK_p may be taken as constant, is capable of direct integration. Thus we have

$$\left(\frac{dv}{dT}\right)_P = \frac{v + CK_p}{T}.$$

Hence, integrating under constant pressure we get from

$$\frac{dv}{v + CK_p} = \frac{dT}{T}$$

the result

$$\frac{v + CK_p}{T} = \text{constant for any particular pressure.}$$

This expression

$$\frac{v + CK_p}{T} = A \text{ (say). } (\epsilon),$$

may be used in a simple manner to determine the specific volume v in superheated steam at any temperature and pressure, the value of A for this particular pressure being calculated from known data of the saturated condition.

It would appear, however, from Section XVI., p. 25, that the maximum volume which steam can occupy at the temperature of saturation under a certain pressure is not that given in the usual steam tables for the volume of dry saturated steam under that pressure and temperature, as the dry saturated steam used in the experiments does not become superheated with the slightest amount of wiredrawing. A correction, which is usually very small, could be found for the specific volume of the dry saturated steam as obtained from tables, to bring it to the specific volume of steam when a maximum at the temperature and pressure of saturation considered, *i.e.*, when no further increase of volume can occur at that pressure without superheating. Thus, taking an actual example, it is shown on p. 25 that at 236.4° the maximum amount of heat the steam can contain at this temperature of saturation without becoming superheated is equal to the total heat of evaporation of the steam at 239.2° F. as given by the steam tables, *i.e.*, the latent heat required to create the maximum volume at 236.4° F. is greater than that required to bring the steam to the dry saturated condition by the amount

$$0.305(239.2 - 236.4) \text{ or } 0.854 \text{ B.T.U.,}$$

and hence the ratio of the specific volume of dry saturated steam to the maximum volume obtainable under the same conditions of pressure and temperature is $= \frac{949.52}{950.374}$, 949.52 being the latent heat of evaporation in B.T.U.s of steam at 236.4 , for, according to RANKINE'S formula for calculating the specific volumes of saturated steam, the volume is proportional to the latent heat.

The maximum volume being obtained in this manner by substituting it in the equation

$$\frac{v + CK_P}{T} = A,$$

it is possible to find A , and hence to find v for any other temperature T under the same pressure, the units of CK_P being altered as required.

By calculations of the preceding nature the volumes have been obtained of superheated steam at various pressures, and at temperatures which enable a direct comparison with HIRN'S experimental results to be made. These experiments of HIRN on the densities of superheated steam do not give very consistent results among themselves, but they are the only ones as yet made which cover such a range of pressure and temperature as is the case in the present research, and hence are the only ones with which a comparison can be made. The experiments of FAIRBAIRN and TATE,* however, furnish us with direct evidence that a very large expansion of

* 'Phil. Trans.,' 1860-2, "On the Law of Expansion of Superheated Steam."

volume takes place between the temperature of saturation and a degree or two above this temperature, and it is probable that this sudden expansion is due to the same cause as that for which the calculation has been made on p. 34, and referred to on pp. 24 and 25, namely, that the volume of dry saturated steam as given in the usual steam tables is not the maximum volume which can exist at that particular temperature of saturation.

The experimental results given by HIRN are placed in the accompanying Table VIII. as affording the only means of comparison as yet obtainable. An examination of this table will show that no great difference exists between the calculated results and those obtained by HIRN, though the constancy of CK_p has been assumed beyond the temperatures obtained in the experiments.

TABLE VIII.—On the Densities of Superheated Steam.*

Pressure in atmos.	Value of A in formula (e).	Temperature.	Calculated sp. volume.	HIRN'S volume.†	Percentage difference.
1	0.04154	212.0	26.43†	26.43†	
		245.3	27.82	27.84	— 0.07
		285.8	29.51	29.64	— 0.44
		299.3	30.07	29.95	+ 0.40
		323.6	31.07	30.91	+ 0.51
		392.0	33.92	33.32	+ 1.77
		401.0	34.29	34.28	+ 0.03
		475.7	37.39	36.66	+ 1.95
2.25	0.019337	392.0	14.98	14.73	+ 1.68
3	0.014944	392.0	11.232	11.165	+ 0.60
3.5	0.013018	384.8	9.495	9.466	+ 0.30
		393.8	9.613	9.668	— 0.57
		437.0	10.175	10.188	— 0.13
		475.7	10.679	10.531	+ 1.39
4	0.011592	329.0	7.642	7.724	— 1.07
		392.0	8.373	8.362	+ 0.13
		437.0	8.894	8.634	+ 2.92
		475.7	9.343	9.214	+ 1.38
5	0.009593	320.0	5.977	6.020	— 0.72
		392.0	6.668	6.558	+ 1.65
		401.0	6.754	6.632	+ 1.81

* In these calculations, the value of J used has been taken as 774, a number recently adopted by Professor PERRY (in 'The Steam Engine'), and more in accordance with recent researches than the number 778.

† PERRY, 'Steam Engine,' p. 577.

‡ Volume of 1 lb. of dry saturated steam in cu. feet as given in steam tables.

II. *A Comparison of Platinum and Gas Thermometers, including a Determination of the Boiling-Point of Sulphur on the Nitrogen Scale. An Account of Experiments made in the Laboratory of the Bureau International des Poids et Mesures at Sèvres.*

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Communicated by the Kew Observatory Committee.

Received and Read June 15, 1899.

[PLATE 1.]

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CALLENDAR employs the symbol pt , its value depending on the sample of platinum chosen.

In order to reduce to the standard scale of temperature the indications of any platinum thermometer, it is necessary to know the law connecting T and pt . These are, of course, identical at 0° and 100° , but the determination of the remainder of the curve expressing the relationship between them is a matter for experiment. Our present knowledge of this relation depends mainly on the investigations of CALLENDAR and GRIFFITHS.

The following is a list of the principal papers published bearing on the subject of platinum thermometry :—

CALLENDAR	'Phil. Trans.,' A, 1887.
"	'Phil. Mag.,' July, 1891.
"	" July, 1892.
"	" February, 1899.
GRIFFITHS	'Brit. Assn. Reports,' 1890.
"	'Phil. Trans.,' A, 1891.
"	" 1893.
"	'Proc. Roy. Soc.,' vol. 55, 1894.
"	'Nature,' November, 1895.
"	" February, 1896.
CALLENDAR and GRIFFITHS . . .	'Phil. Trans.,' A, 1891.
CAREY FOSTER	'Nature,' August, 1894.
HEYCOCK and NEVILLE . . .	'Chem. Soc. Journ.,' 1890.
"	" 1895.
GRIFFITHS and CLARK	'Phil. Mag.,' December, 1892.
CLARK	'Electrician,' vol. 38.
OLSZEWSKI	'Phil. Mag.,' August, 1895.
DEWAR and FLEMING	" September, 1893.
"	" July, 1895.
HAMILTON DICKSON	" December, 1897.
"	" June, 1898.
D. K. MORRIS	" September, 1897.
WAIDNER and MALLORY	" August, 1897.
DAY	" August, 1897.
CHREE	'Nature,' July, 1898.

The work of CALLENDAR established for a particular sample of pure platinum the relation

$$d \equiv T - pt = \delta \left[\left(\frac{T}{100} \right)^2 - \frac{T}{100} \right]$$

over the range 0° to 600° . For CALLENDAR's wire the value of δ was about 1.57.

Subsequent experiments by CALLENDAR and GRIFFITHS showed that the values

of δ for the different samples of platinum they examined varied greatly with their purity, yet, provided that the percentage of impurity were small, the formula given above held true. They found from their experiments that the $T - pt$ curve was always a parabola, and that, therefore, to establish the whole curve showing the divergence of the two scales, it was sufficient to know d for three fixed points. For two of these, viz., 0° and 100° , d is by definition zero. For the third point, for reasons indicated in their paper, GRIFFITHS and CALLENDAR chose the boiling-point of sulphur, and subsequently made a new determination of this point by an air thermometer, finding as their most probable value $444^\circ\cdot53$, the pressure being 760 millims. This value, which is nearly four degrees lower than that previously obtained by REGNAULT, is the one which has been generally adopted in work with the platinum thermometer.

As further evidence in confirmation of this conclusion GRIFFITHS points out that, if this number be taken for the boiling-point of sulphur in the calculation of the values obtained by him for the boiling and freezing points of a number of substances on which he experimented, the results for most of the substances concord better with their accepted values as determined by other observers, than if REGNAULT'S value, $448^\circ\cdot34$, be adopted.

Many of these accepted numbers quoted in GRIFFITHS' paper are given to hundredths of a degree, but closer examination of the original papers in most cases reveals the fact that the reductions to the normal scale and the various corrections of the thermometers employed, if made at all, are, to say the least, very uncertain. Further, we see no *a priori* reason why, in GRIFFITHS' experiments, the results with certain of the substances employed should be rejected from consideration, as there does not appear sufficient ground for supposing that the experimental error in these cases was higher than the average.

Substantially then our knowledge of temperatures, deduced by means of the platinum thermometer, depends solely on the correctness of the conclusions of GRIFFITHS and CALLENDAR:—

- (1) That the boiling-point of sulphur under 760 millims. pressure is $444^\circ\cdot53$.
- (2) That the curve representing the divergence of the platinum and air scales is a parabola.

II. THE INVESTIGATION FOR THE KEW COMMITTEE.

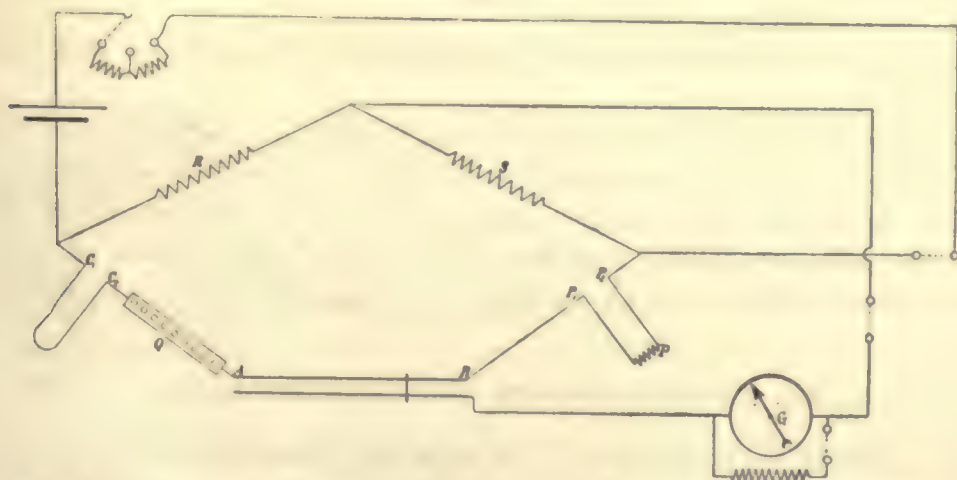
In recent years the platinum thermometer has been employed by various observers, and their experience has tended to confirm the view that it could be relied upon to give constant indications at a given temperature. It consequently appeared to the Kew Observatory Committee that it might be possible to use this instrument as a means of referring measurements of temperature to the scale of the gas thermometer adopted as an International standard by the Comité International des Poids et Mesures, and thus to extend their means of accurately testing thermometers sent to

them for verification at temperatures outside the range 0° to 100° . With this view they deemed it desirable to obtain an independent investigation into the principles and methods of platinum thermometry, and they consequently procured a complete equipment of the necessary apparatus, which was installed at the observatory under the supervision of Mr. GRIFFITHS in a special building. As the general results of the experiments made with this apparatus seemed promising, the Kew Committee approached the Comité International des Poids et Mesures, with a view to securing their co-operation, and ultimately it was arranged that a direct comparison, extending over as wide a range as possible, should be made between some platinum thermometers belonging to Kew and the Standard instruments at the International Laboratory at the Pavillon de Breteuil, at Sèvres, near Paris. The present paper is the outcome of this investigation, in which it may be understood that one of us (C.) is responsible for the gas and mercury thermometry involved, while the working of the platinum thermometers devolved on the other (H.). In it will also be found an account of the means by which the range of the gas thermometer employed was extended upwards from 200° , the limit of the Bureau's previous experiments, for the purpose of this investigation.

III. THE FIRST FORM OF PLATINUM THERMOMETER RESISTANCE-BRIDGE.

As a full account of the first platinum thermometer apparatus acquired by Kew Observatory has been published by GRIFFITHS ('Nature,' Nov. 14, 1895), under whose supervision it was standardized, it is unnecessary here to give more than a general description of its chief features. A diagrammatic representation of the connections is given in fig. 1.

Fig. 1.



Q Resistances of bridge.
R and S Proportional coils.
P Thermometer spiral.

C Compensator of thermometer.
AB Bridge-wire.
G Galvanometer.

Here R and S represent the proportional coils of about five ohms each, adjusted to exact equality. P is the thermometer coil connected by two long flexible copper ends to the box terminals P_1 and P_2 .

The wires in the stem of the thermometer leading to the coil are of thick platinum, the coil itself being of a very pure sample of platinum .006 inch in diameter. Down the stem run also a second pair of leads made as similar as possible to the coil leads, but connected together at their lower extremities and having no contact with the coil. This loop, connected at C_1C_2 in the figure in the opposite arm of the bridge to the thermometer itself, serves to compensate the changes in resistance of the thermometer leads proper, due to variations of stem temperature. The four copper wires joining P_1P_2 , C_1C_2 to the thermometer are plaited together into a single cable, so that temperature changes throughout their length may affect them all equally.

Q represents the nine platinum-silver resistances of the box connected to one another in series, the lowest coil having a resistance of 5 box-units (1 box-unit = .01 ohm), and the rest forming a series 10, 20, 40, 80, up to 640 units the largest coil. An extra coil of 100 units is used to determine the fundamental interval of the usual type of thermometer, whose change of resistance between 0° and 100° is 100 box-units, i.e., 1 ohm.

A platinum silver bridge-wire, AB, provided with a scale of millimetres, furnishes the means of balancing exactly any resistance of P. A special form of slider is employed for the contact between the bridge-wire and a precisely similar wire stretched parallel to it, connected to the galvanometer. The exact position of the transverse wire forming the contact-piece is indicated by a vernier by which .01 millim. may be estimated. This symmetrical arrangement of two similar wires is found to diminish the thermoelectric effects at the movable contact.

Coils of 20 and 100 ohms are provided as resistances in the battery circuit, and also a "tenth" shunt for the galvanometer.

The top of the resistance-box is of a special quality of marble of good insulating properties.

The whole is enclosed in a double-walled tank holding a considerable mass of water, which is kept at a constant temperature near 20° , by a regulator controlling a small gas flame. A delicate thermometer suspended in air in the interior of the box indicates the coil-temperature, and the whole of the upper surface of the box is protected against radiation and air currents by a glass cover similar to a balance case.

IV. EXPERIMENTS WITH THE FIRST APPARATUS.

From the time of the acquisition of this apparatus determinations were repeatedly made of the constants of each of the platinum thermometers, in order to test the permanence of the whole arrangement under ordinary working conditions; also to ascertain how the accuracy obtained was influenced by alterations in the external

conditions of experiment, such as changes in the laboratory-temperature, the different treatment of the apparatus by different observers, &c.

These trials, which were continued over a considerable period, showed that one of the disadvantages of this form of apparatus is the almost inevitable difference of "lag" between the mercury thermometer employed to indicate the coil-temperature, and the platinum-silver coils themselves, which in this case hang loosely in air. From this cause, especially when the box-temperature is changing rapidly, some uncertainty as to the coil-temperatures is introduced. During the winter, when the temperature of the laboratory often fell very considerably during the night, and also in summer when it rose to over 20° , the temperature of the *coil-space* changed rapidly during the daytime, although the regulator nevertheless maintained the water in the tank very near 20° throughout, showing that the protection afforded by the glass cover of the resistance-box was insufficient under the prevailing conditions. The measurements made showed conclusively that in this case the coils followed temperature changes *faster* than the mercury thermometer selected to indicate the coil-temperature.

The temperature-coefficient of the alloy of which the coils are constructed is $\cdot 00026$ and that of the platinum wire of the thermometers is $\cdot 00386$; if then we wish to determine a platinum-temperature to $\cdot 001^{\circ}$ (whatever the resistance of the thermometer chosen) we must know the coil-temperature to $\cdot 015^{\circ}$. Therefore, unless great precautions be taken with the mercury thermometer, it is difficult to see how the measurements of coil-temperature can be sufficiently trustworthy.

GRIFFITHS in his later experience has got rid of the first-mentioned difficulty while retaining platinum-silver as the resistance metal, by immersing the coils in a well-stirred bath of highly insulating oil, into which the mercury thermometer is placed directly, thus rendering the measurement of the coil-temperature much more certain.*

V. CONSTRUCTION OF THE NEW APPARATUS.

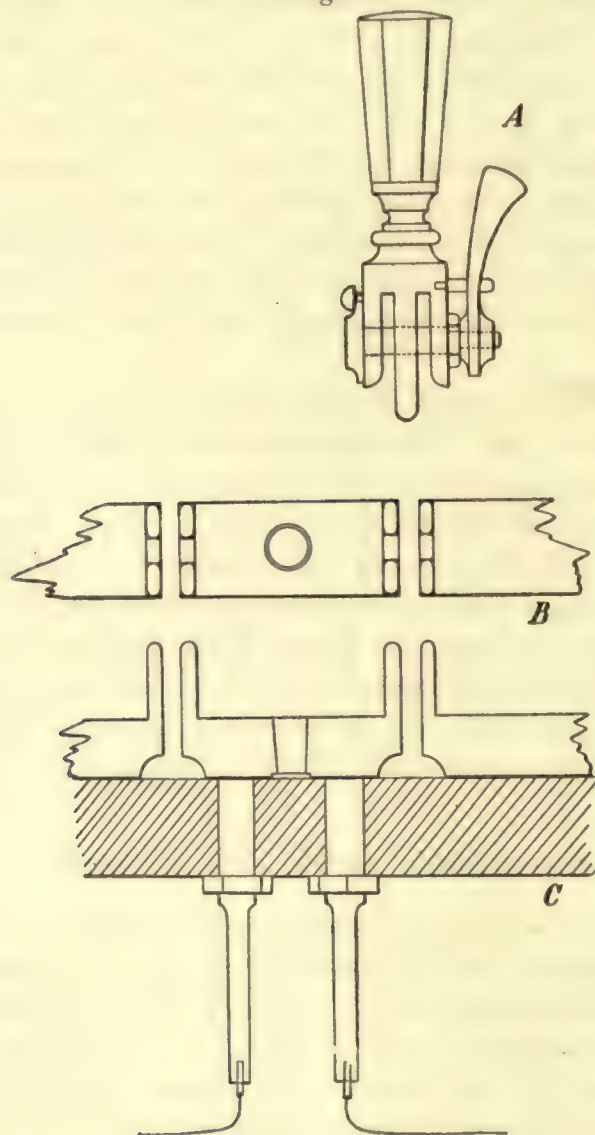
As it was anticipated that the experiments at Sèvres might occupy some time, and it was not thought advisable that the Observatory should be deprived altogether of the use of platinum thermometers for a long period by this apparatus being taken to France, a new resistance-box was ordered specially for this work. The construction of this box was entrusted by the Committee to Messrs. CROMPTON and Co., Limited, and its behaviour has on the whole been very satisfactory.

In view of the fact that it was not easy to maintain the platinum-silver coils at a sufficiently uniform temperature winter and summer by any simple means, and in view of the difficulty previously mentioned as to the indication of the true coil-temperature with sufficient accuracy by a mercurial thermometer, it was decided in

* A description of GRIFFITHS' subsequent improvements on the original Kew apparatus, here described, is given by G. M. CLARK ('Electrician,' vol. 38, p. 747).

this second apparatus to obviate the necessity of very accurate measurement of the coil-temperature by using one of the new alloys of very small temperature-coefficient, manganine being the one chosen. The expediency of this change was subsequently emphasised by the fact that we found it was inadvisable to artificially heat the room at Breteuil in which the comparisons were made, on account of the uncertainties

Fig. 2.



attending the measurement of the temperatures of the various mercury columns of the gas thermometer. During the year and a-half the experiments lasted, the room temperature varied from about 4° to 23° , which would have rendered accurate artificial control of the box-temperature extremely difficult.

Since in the first resistance-box the thermoelectric effects between the various wires and terminals in the circuit (in which several different metals are used) were

sometimes considerable, copper was substituted throughout for brass in the new box, the only metals in circuit being copper and manganine. For the platinum-silver bridge-wire was substituted a manganine strip heavily gilt, placed on edge and stretched between two adjustable clips. The slider is provided with a fine adjustment, which can be manipulated *from the outside of the box*, without risk of heating the galvanometer-contact by repeatedly approaching it with the hand. As in Mr. GRIFFITHS' latest form, the terminals project outside the glass case. The top of the box is formed of a heavy slab of white marble 75 centims. long, 30 centims. wide, and 3 centims. thick. For the ordinary form of plug-contacts are substituted heavily gilt forks of forged copper, which can be clamped by powerful steel screws over tongues projecting upwards from the blocks to which the coils are fastened. A general plan of the resistance-box is shown in Plate 1 and the details of one of the contacts in fig. 2.

VI. THE RESISTANCE-COILS.

The general scheme of the box connections is almost the same as the one previously described, and may be traced in fig. 1. For the winding, fixing, and annealing of the manganine coils the method described in the official publication of the Physikalisch-Technische Reichsanstalt at Charlottenburg was carefully followed. The specimen of wire used was selected after various tests from several furnished by Messrs. W. T. GLOVER and Co., of Salford, and was double silk covered No. 26 S.W.G. The diameter of several pieces cut from different parts of the bobbin only varied within very narrow limits. In order to simplify the application of the temperature correction, the same wire was employed for all the coils except the two lowest. These were of strip manganine, and being originally cut off too wide, could be adjusted till accurate by clipping the edge with shears.

VII. COIL VALUES ADOPTED.

In the Callendar-Griffiths resistance-boxes the coils are arranged on the binary scale, and the value of each is determined in terms of the sum of those below it together with a certain length of bridge-wire. Although Mr. GRIFFITHS gives evidence for the utility of this arrangement in general work, it was thought more important, for the purposes of this research, to have several independent checks in the determination of each coil-value, than that the maximum resistance, measurable with a given number of box-coils, should be as high as possible.

The thirteen coils were therefore arranged as follows, the values being expressed in ohms :—

40	20	10	4	3	2	1
A	B	C	D	E	F	G
·02	·05	·1	·2	·3	·4	
N	M	L	K	J	H	

Several of these values are the ordinary ones adopted for standard resistances, so that with a suitable arrangement comparisons with a standard could be made from time to time. Coils of these values are also much easier to measure off accurately than the larger multiples of .01 ohm on the binary scale. We will revert to this question as to the best arrangement of coil-values in the discussion of the method of standardization adopted.

The resistance box is fitted with three interchangeable bridge-strips of different resistances, on which a change of .01 ohm in the box-coils causes a displacement of the slider, to restore the balance, of 10, 5, and 2 centims. respectively. The slider is fitted with a vernier giving $\frac{1}{10}$ th millim. directly, it being considered unnecessary, perhaps indeed impossible, to determine the position of the knife edge forming the contact to a greater accuracy than this, without taking extraordinary precautions with the scale, the slider, and the bed in which it travels.

With the three bridge-strips the resistance corresponding to a movement of one millim. is .0001, .0002, .0005 ohm, respectively.

The strip of medium resistance was the one employed exclusively during this research.

The slider is of the form employed on the best potentiometers, and can be displaced either by hand or by a fine-adjustment screw with large milled head, projecting beyond the outside of the case. This screw moves longitudinally a rectangular frame carrying the slider; this frame is also capable of lateral movement in the massive brass casting which surrounds the bridge-wire, and tends to protect it from injury, and to equalise its temperature from end to end. The return contact from the slider to the galvanometer was originally made by means of this movable frame, but from some unexplained cause, apparently not thermoelectric, this led to unsteadiness of the galvanometer zero.* Coupling the various parts of the framework together electrically by flexible copper wires did not remove the difficulty, and ultimately it was found best to have a silk-covered return lead attached to the spring contact on the slider, and to cut off the frame from all electrical connection with the apparatus.

The marble slab forming the top of the resistance-box was supported from the inside of the tank by an iron framework, carrying racks for the coils, the sides being left quite open, and all the coils easily accessible for inspection at any time. The whole was placed in a very heavy double-walled copper trough holding about 50 litres of water, and was covered by a doubly-hinged lid, glazed with thick bevelled plate

* In these experiments, in which a Griffiths' thermoelectric key (described later) is used, in the normal position of the key the galvanometer circuit remains *made*. When the platinum thermometer is not changing rapidly in temperature, the stability of the galvanometer zero is a good criterion, from which much may be gathered as to the working state of the bridge, and the magnitude of the thermo-currents present. We have reason to believe from our own experience that the use of a well-constructed key of this type considerably facilitates the carrying out of low-resistance measurements, where high accuracy is desired.

glass. Provision was made in the outer space of the tank for a regulator and heating arrangement underneath. This was, however, not used during the present experiments. Suitable thermometers indicated the temperature of the water in the outer tank, and two sensitive ones, divided to tenths of a degree with thin bulbs and their stems bent at right angles, indicated the temperature of the internal coil-space.

IX. GALVANOMETER SHUNTS AND BATTERY RESISTANCES.

The resistance-box was provided, as in the Callendar-Griffiths type, with a set of galvanometer shunts and a series of battery resistances of 20, 50, 100, and 500 ohms. It was afterwards found a great advantage to have a more exact adjustment of the battery current, and for this purpose a subsidiary three-dial box, working up to 1,000 ohms, was provided.

Previous experience at Kew had shown the occurrence of differences in the point of balance, according as the battery-current was in one direction or the other; it was found that the difference between the readings with the current in the two directions generally increased gradually during the first quarter of an hour on commencing the observations, and was greater the greater the intensity of the battery current. In order to be able to study, and if possible to eliminate this cause of uncertainty, we placed in the battery circuit of the new apparatus a high-insulation reversing switch. The working of this switch was at first unsatisfactory, but was subsequently perfected by short-circuiting the rubbing contacts at the pivots by flexible brass strips, and covering the five contact studs with thin platinum plates.

X. BATTERY POWER EMPLOYED.

The battery used throughout the experiments consisted of two dry-cells of the Obach type, obtained from Messrs. SIEMENS; we ascertained that the E.M.F. of the two cells was practically constant throughout and about 2.8 volts, and that the internal resistance of the two in series did not rise to more than 1 ohm, changing by a quantity quite negligible in comparison with the large resistance always added in the battery circuit.

XI. THERMOELECTRIC KEY.

For the completion of the different circuits a Griffiths' thermoelectric key was employed, as in the first Kew apparatus. The essential feature of this key consists in the addition to the ordinary form of double bridge-key of a lever so arranged that when the key is released the galvanometer circuit remains made. Thus a simple depression of the key first breaks the circuit of the galvanometer, then makes that of the battery, and finally remakes the circuit of the galvanometer.

The key we used was somewhat modified from the original pattern, which, being

mounted on wood, was not found to be quite perfect as regards insulation. The new key, which along with the thermometers and nearly all the accessory apparatus was obtained from the Cambridge Scientific Instrument Company, Limited, is shown in fig. 3, and in the general plan of the auxiliary apparatus (fig. 4). It is provided with

Fig. 3.

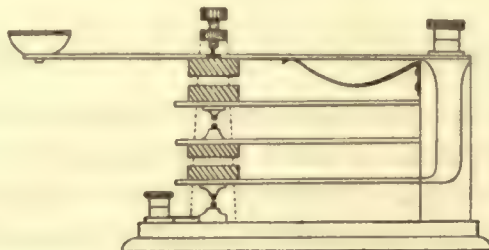
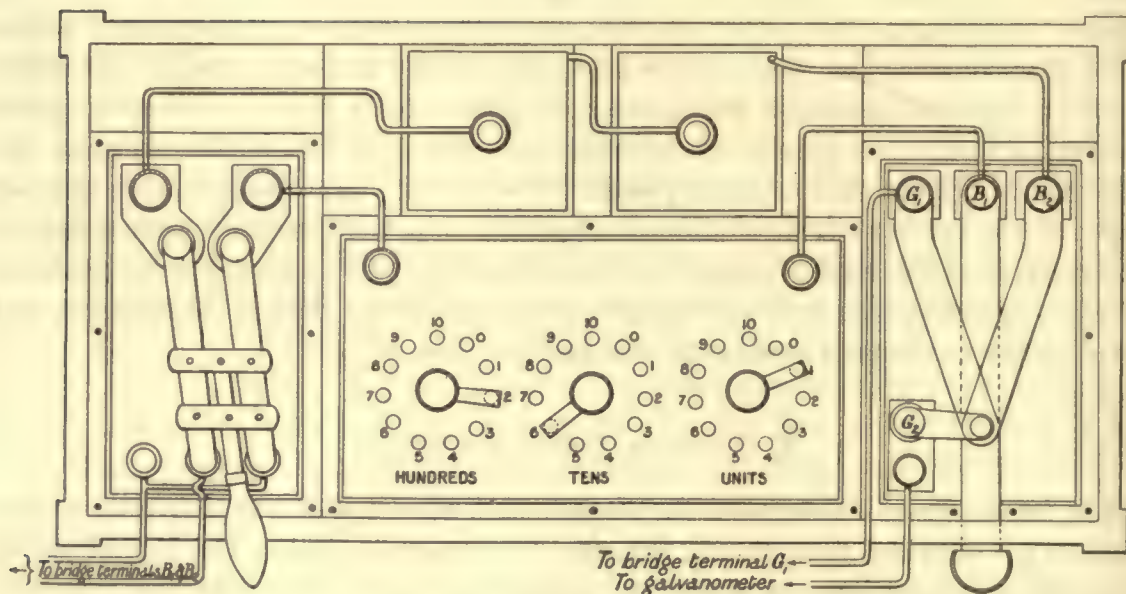


Fig. 4.



ebonite pillar insulation, and the four levers are rearranged in their order, the two forming the galvanometer-contacts being supported from the same pillar one under the other. All the contacts in the key are of platinum. An adjustable steel spring under the topmost lever helps to hold it up against the contact screw above, thus ensuring good contact in the galvanometer-circuit when the key is released.

XII. ACCESSORIES TO THE RESISTANCE-BRIDGE.

The battery, reversing-switch, key, and external resistances were all enclosed in a wooden case provided with a glass lid, the necessary handles for the adjustments and for working the keys, projecting through the sides, and the whole being kept nearly

air-tight by suitable protections. This seemingly unimportant detail we found to be a great advantage, as in the damp weather, experienced during part of the experiments, the insulation of exposed parts always required considerable attention. The battery was insulated from the wooden case by gutta-percha strip, and after this was added, the insulation resistance of the whole apparatus, when all was kept dry, was practically perfect.

XIII. GALVANOMETER.

For the first experiments the galvanometer employed was one of the pattern described by DUBOIS and RUBENS in 'Wied. Annalen,' vol. 48, p. 236, lent to us by Professor SCHUSTER. This is a Thomson four-coil instrument with connections so arranged that its bobbins may be coupled to give an internal resistance of 80, 20, or 5 ohms. The magnet system and mirror weighed together 0.2 gram. The deflections were observed from about three metres distance by a large Steinheil telescope. Much trouble was experienced in finding a foundation for the galvanometer sufficiently free from vibration. After several unsuccessful experiments in which we attempted to insulate the galvanometer with rubber blocks, a special pillar was erected independent of the floor. We found, however, that, even when resting on this, the vibration of the magnet-system, caused by heavy traffic on the Versailles road, was sufficient at intervals to prevent any satisfactory observations being made. At this juncture Professor CAREY FOSTER was appealed to, and through him Mr. R. K. GRAY, of the India-rubber, Gutta-percha, and Telegraph Works Company, of Silvertown, very kindly came to our aid by sending us a reproduction of an arrangement he had employed at the works to cut off vibrations from delicate instruments. It consisted of a brass plate forming a platform from which the galvanometer is suspended, the whole being slung by long india-rubber tubes from a wall-bracket above. To diminish the effect of air currents we added a damping arrangement consisting of a vertical metal cross with attached horizontal vanes, plunging into a vessel standing on the concrete pillar and containing a thick oil. The galvanometer and suspension were also completely surrounded by a paper screen extending upwards to the ceiling, provided with suitable openings for making the adjustments.

The india-rubber suspension arrangement, when once the tubes were properly stretched, worked perfectly satisfactorily till the winter, when, presumably under the influence of the low temperature of about 4° or 5° , such a change took place in the elasticity that we were obliged to seek a substitute for the india-rubber, less influenced by climatic conditions.

We at length managed to construct from steel wire, 1 millim. in diameter, long spiral springs of the requisite strength, which have served the purpose admirably, and at the same time have shown a comparatively small variation of elasticity with temperature. The arrangement of the suspension in its modified form is shown in figs. 5 and 6.

Fig. 5.

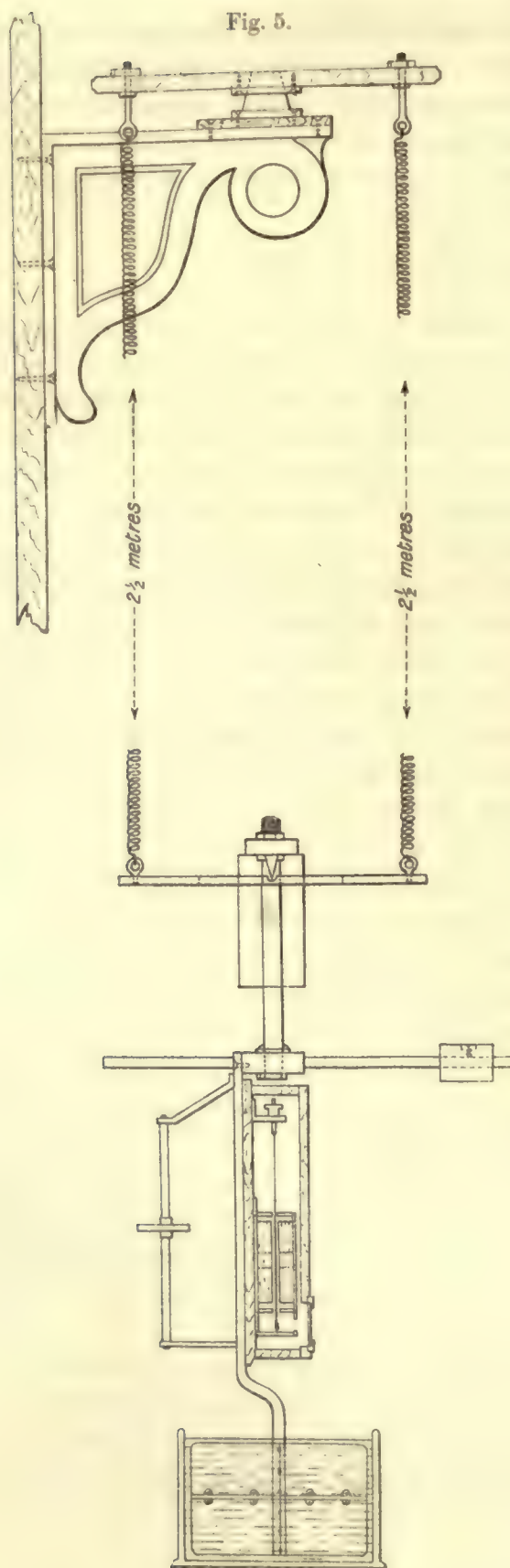
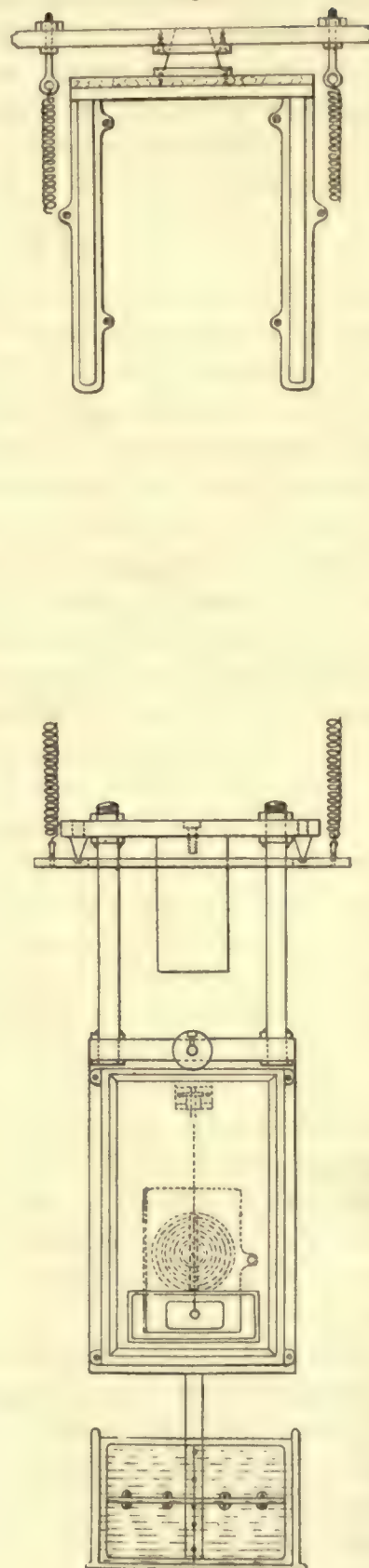


Fig. 6.



With the comparatively heavy magnet-system of this first galvanometer, we were obliged, in order to obtain the requisite sensibility, to work with a relatively long time of vibration, which was not convenient for rapid work, and it was ultimately found necessary to so modify our galvanometer that the necessary sensitiveness should be obtained with a time of swing not exceeding six or seven seconds. We therefore had recourse to the ingenious type of magnet-system devised by M. BROCA, of the Ecole de Médecine, Paris, and described by him in the 'Journal de Physique,' February, 1897. In its latest form this consists of two vertical hollow magnets, having at their middle points a north and south pole respectively. When the two similar but oppositely magnetised needles are fixed strictly parallel to one another, the system thus formed is perfectly astatic in a uniform field, since the strength of the pole at the centre of each magnet is equal to the sum of the poles at its ends, and further the astaticism is not affected by even complete loss of magnetism in one of the magnets. M. BROCA was kind enough to lend us a galvanometer of the type described in his paper, and a magnet-system made by himself. This instrument is the one shown in the sketches of the galvanometer and suspension in figs. 5 and 6. We had not the means of accurately measuring the sensitiveness of this instrument by one of the ordinary processes, but ascertained that, with a time of swing of five seconds, the scale deflection, for a want of balance of the bridge corresponding to $\cdot 001^\circ$, was about 0.5 millim. This was with a system carrying a mirror large enough to give a bright image in the telescope, readable without difficulty in broad daylight.

XIV. THERMOMETER LEADS.

The thermometer leads were of stranded copper equal to No. 17 S.W.G., and about seven metres long. The resistance of the four separate wires was carefully equalised before fixing on the copper end-pieces used to make the contacts, each loop, P_1P_2 , C_1C_2 , having a resistance of $\cdot 15$ ohm at 16° . After nearly two years continual use the two loops differed in resistance by $\cdot 0003$ ohm, a change of only about one-fifth per cent. of the whole.

The connections between the resistance-box leads and thermometer were made by means of the special alloy employed by Mr. GRIFFITHS, and from our own experience we can strongly recommend these joints as very trustworthy and easy to make.

XV. THE PLATINUM THERMOMETERS.

The resistance of all except one of the platinum thermometers belonging to the original Kew installation was such that their change of resistance between 0° and 100° was almost exactly one ohm. Though convenient for high range work, this type of thermometer is hardly suitable for measurements of the highest accuracy at lower temperatures, in consequence of the relatively considerable effect on the results of

small variations in the plug-contact resistances. On this account two new thermometers of higher resistance were ordered from the Cambridge Instrument Co.; their fundamental intervals were five and ten ohms respectively. They are designated in this paper K. 8 and K. 9.

Owing to the shape of the various baths in which the comparisons with the platinum thermometers were made, and more especially to the difficulty of keeping dry the air within the tubes of thermometers of the old form, we were obliged to modify the form of the "head" of these principal thermometers.

In the reconstruction the whole thermometer was arranged so as to be practically air-tight, and the contacts were rearranged in such a manner that although the four wires all left the thermometer at the same side, yet the "coil" and "compensator" arms were perfectly symmetrical. At the same time the number of contacts where thermoelectric effects could arise was reduced as far as possible, by suppressing the brass terminals and making the connection between the platinum leads and the copper fusible metal cups *directly* by stout copper wires, all joints being made quite secure with hard solder. Though this form of thermometer-head is a little more difficult to construct, we find when the four contact cups are surrounded by a thin shield of polished metal to keep off air-currents, that the thermo-effects, almost invariably present to *some* extent in the old form of thermometer, especially when rapid temperature changes are progressing, are almost entirely absent. Another feature is the readiness with which the glass tube can be freed from internal moisture by simply

Fig. 7.



connecting the small stopcock on the ebonite plate alternately to a vacuum pump and to an arrangement for supplying dry air, while the whole thermometer is at a high temperature. This we find to be of great importance for accurate work below 100° .

A sketch of the thermometer in its improved form is given in fig. 7.

XVI. STANDARDIZATION OF THE RESISTANCE-BOX.

The standardization of the resistance-box consisted in the determination :—

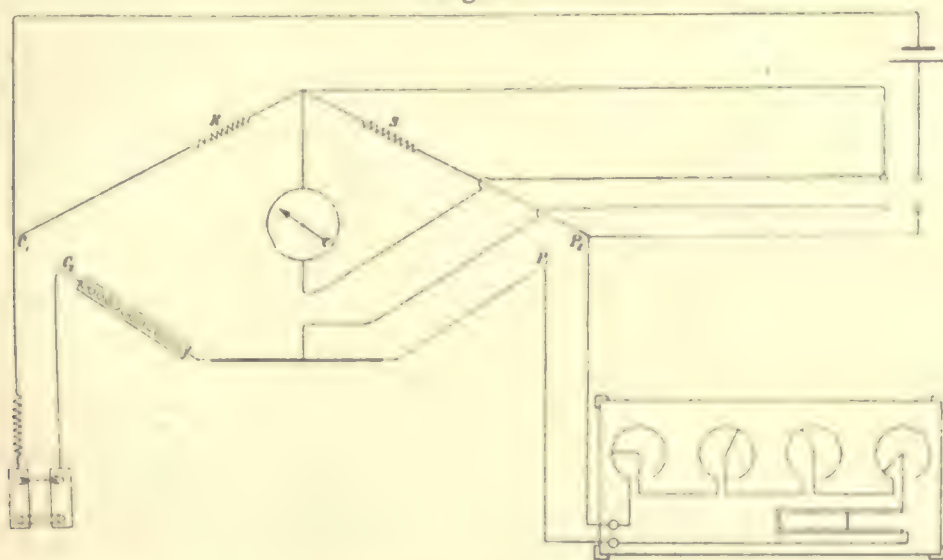
- (1) Of the calibration corrections of the bridge-wire ;
- (2) Of the values of the resistance coils in terms of one another ;
- (3) Of the temperature-coefficient of the coils.

XVII. Calibration of the Bridge-Wire.

As has previously been mentioned, the cylindrical bridge-wire employed in the

CALLENDAR-GRIFFITHS box was replaced by a manganine strip, cut from a large sheet. Although this strip had been carefully adjusted by filing to a very fairly uniform resistance along its whole length, yet, from the method of its construction, we anticipated the possibility of there being in some places more sudden variations of resistance than were likely to occur in a wire of a hard material like platinum-silver or platinum-iridium carefully drawn down to a certain diameter. We determined therefore to substitute for the usual GAY-LUSSAC calibration a more complete one with several different "columns." As it was not always possible to take vernier-readings with the slider close up to the ends, we decided to employ only the middle 48 centims., and to obtain the calibration corrections for each 2 centims. over this range. We are indebted to Dr. BENOIT for his advice on the best method to adopt. He recommended that the whole length should be divided into two parts, and that for each part a "complete" calibration should be made for every 4 centims., involving the employment of "columns" of 20, 16, 12, 8, and 4 centims., and that afterwards the intermediate 2 centim. points should be determined by subdivision of each interval of 4 centims. into two parts. The necessary conversions of the separate corrections found to one system were made exactly as in the calibration of a mercury thermometer or a divided scale.

Fig. 8.



The method adopted for making the necessary measurements is described in a paper presented to the Royal Society in 1896 by one of us; the scheme of the connections is shown in fig. 8.

Between the terminals P_1P_2 of the resistance-box is connected an auxiliary adjustable resistance, having four sets of coils made of the same sample of manganine as those of the bridge proper, and also a small U-shaped trough containing mercury. By means of this appliance, a plan of which is shown in fig. 9, the resistance between

Fig. 9.

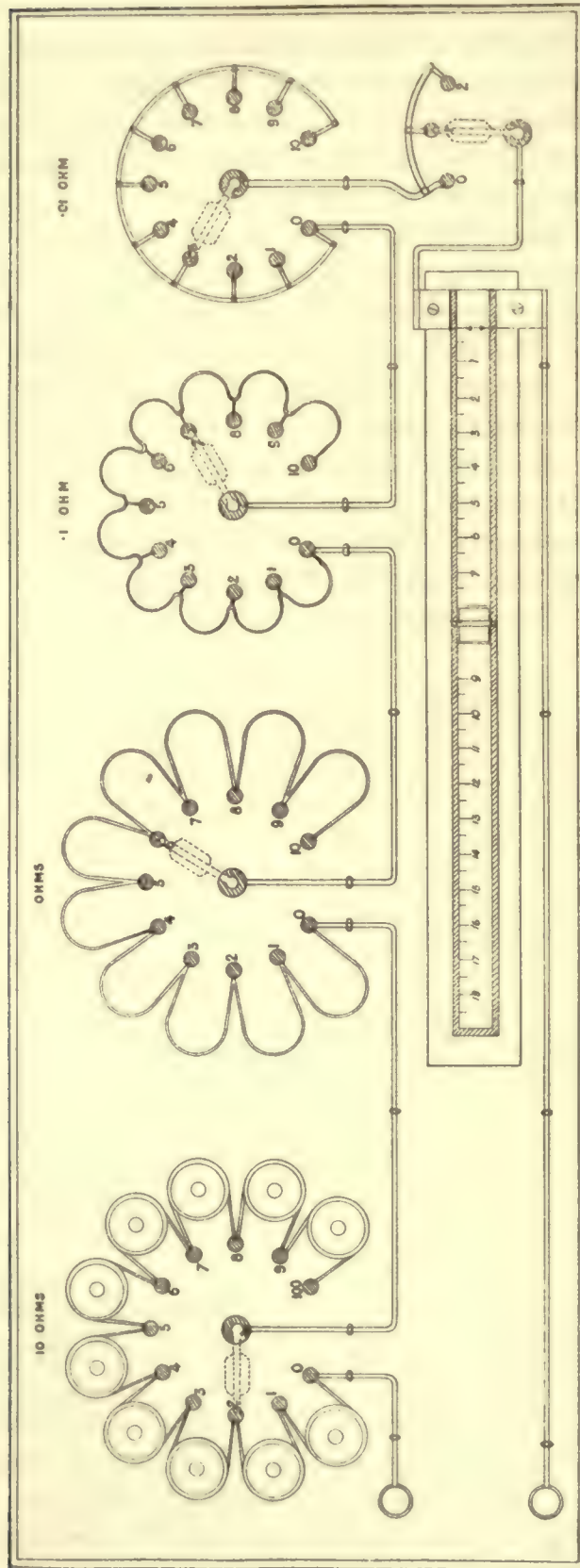
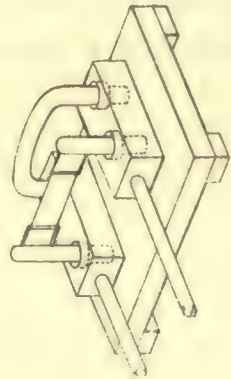


Fig. 10.



the terminals P_1P_2 can be quickly adjusted to any value between zero and 100 ohms. In the opposite arm of the bridge, between the terminals C_1C_2 , are inserted a fixed resistance of 0.1 ohm and the calibrating apparatus. This consists of two massive copper blocks of rectangular form, mounted on an insulating base, each pierced by two holes about a centimetre in diameter, which are well amalgamated and partly filled with mercury. Into one pair of holes are inserted two round copper pillars, across which is soldered a piece of thin manganine strip, and into the other pair of holes the lower ends of a thick U-shaped copper rod. A sketch of the calibrator is given in fig. 10.

A number of strips of different resistances, each mounted between copper pillars as shown, are first prepared, the values chosen being equivalent to 2, 4, 8, 12, 16, 20, and 24 centims. movement of the slider. The calibration is commenced by placing the contact-maker to the division 24 to the left, and one of the strips in position on the calibrator. The resistance in the opposite arm of the bridge is then adjusted so that no galvanometer deflection is obtained, and the exact position of the slider noted. The manganine strip remaining untouched, the copper short-circuiting piece is now placed across between the two remaining mercury cups, and the slider is then moved to the right till the balance is again restored. In order to eliminate the effects of any gradual temperature changes, the process is repeated, the readings being made in the reverse order, a similar pair of readings being made for each successive position along the bridge-wire. The results of several series of observations made on different days with each strip are then combined, and the whole set treated precisely as an ordinary calibration of a length or volume, and the curve of corrections prepared.

It was interesting to compare the results of the complete calibration with those deduced from the observations with the two-centim. column alone, and from two test calibrations made by means of the coils M and N. The general agreement of the different results was found to be satisfactory.

XVIII. *The Resistance Coils.*

The manganine coils were annealed, in accordance with the recommendations of the German Reichsanstalt, by heating them to about 140° for some time and allowing them to cool slowly. This was done in a closed electrically heated space in which the temperature could be regulated at will, and the cooling could be made as slow as desired.

The ends of each coil were hard-soldered to copper tags of rectangular form previous to the final annealing, these tags being afterwards firmly fastened by ordinary solder to the stout tinned copper leads connected to the contact-blocks.

The coils were wound on glass tubes 3 centims. in diameter, which were fastened by metal strips to wooden cross-pieces supported from the iron framework of the resistance-box. These tubes were coated with three thin layers of shellac varnish

before the coils were wound, and after the winding the wire itself was also well varnished to improve the insulation and to protect it from oxidation during the annealing.

We understand that the standard manganine coils issued by the Reichsanstalt are not tested till a year after their construction, but that after this lapse of time the gradual changes they exhibit are very small.

In our case we were however obliged to begin work with the resistance-box before the coils had been properly aged, and therefore were not surprised at alterations in their values, particularly during the first few months.

We regret that at the commencement of our work we had not at our disposal the means of comparing the coils with an invariable standard, but could only obtain their relative values in terms of the mean bridge-wire unit, which was even more likely to change slightly than the coils themselves; on this account we are unable to give details of the progressive alterations in their absolute values, and can only indicate the means we adopted to prevent these changes influencing the accuracy of our temperature-measurements. The changes were, as was to be expected, most appreciable at the beginning of the work. The first standardization was made as soon as the apparatus was got into order and fitted up at Breteuil, and immediately following this came the comparisons of K. 8 with the mercury thermometers. As soon as this series of comparisons was completed a second standardization was at once made. The individual observations of the thermometric fixed points and comparisons were then reduced with both the earlier and new coil-values. At a later stage it was found that, although the absolute value of the mean bridge-wire unit had slightly altered, yet the values of the box coils relatively to one another, with the exception of one of the very low resistances constructed of strip manganine, had not changed by an amount large enough to make the two determinations differ materially. It was easy to allow for such small variations as did occur by taking into consideration the date of each experiment and assuming that the change between the two standardizations was proportional to the time which had elapsed since the first.

Not counting a preliminary series of observations, four complete standardizations were made in all during the course of the work with the thermometers, and we think that no serious errors were introduced into the results by the alterations in the relative values of the resistance-coils.

Further particulars as to the changes in the values of the different coils are given on p. 58 after the description of the method adopted for the standardization.

For the comparison of the coil-values with one another the following plan was adopted. Firstly, the values of the smaller coils M and N were determined directly in terms of the bridge-wire by the same process as was employed in the calibration. Next, each higher coil in turn was balanced against the adjustable manganine resistance previously described, which in each case was so adjusted that the position of the contact-maker on the bridge-wire was in the neighbourhood of the zero of the

scale. The coil in question was then changed for some combination of those of lower values giving the same (or very nearly the same) nominal resistance, and the outside resistance remaining untouched, the contact-maker was again adjusted to equilibrium.

The distance between the first and second positions of the slider is a measure of the difference between the two sets of coils, expressed in mean bridge-wire divisions. The process being repeated for all the coils and the different combinations equivalent to each, the results are collected into a set of equations of the following form* :—

$$\begin{array}{rcl}
 A - B - C - D - E - F - G & & = a_1 \\
 & \text{\&c.} & \\
 D - E & - G & = a_4 \\
 D - E & - H - J - K - L & = a_5 \\
 & \text{\&c., \&c.} &
 \end{array}$$

As previously mentioned, the scheme of coil-values adopted was such as to permit of independent values for most of the coils being obtained in a single standardization, the difference between these several values being a measure of the accuracy obtained.

For the standardization we adopted the same scheme in the four sets of determinations of the coil-values taken at different times throughout the research. We ascertained during the experiments, but too late to make any change, that the values chosen for the higher coils were not such as were best adapted for giving a number of inter-dependent relations, and on this account the control only extended upwards to the fourth largest coil.

We give below the residual errors obtained in one of the standardizations by substitution of the values found by least squares for each coil in the respective equations of condition, suppressing the first three coils for which the control was absent.†

* The method of forming these equations will be readily seen on reference to the table of coil-values given previously on p. 45.

† In the opinion of Dr. BENOIT, whose kindness in giving us his advice with regard to the methods of standardization we here gratefully acknowledge, the best way to obtain in one standardization the requisite number of equations from which the relative values of such a system of coils can be satisfactorily determined, is to adopt a system similar to that employed for standard sets of weights. After careful consideration of these we think the following scheme for a set of fifteen coils would be almost an ideal one. Without counting combinations only involving changes in coils, whose resistance is small compared to the total in any comparison, we should have in this system several controls for each coil-value

$$\begin{array}{ccccccccccc}
 20' & 20'' & 10' & 10'' & 5 & 2' & 2'' & 1' \\
 \cdot 05'' & \cdot 05' & \cdot 1 & \cdot 2'' & \cdot 2' & \cdot 5 & 1''
 \end{array}$$

The system of about 44 equations of condition to determine the unknowns, given by the different direct comparisons, can either be divided into groups and solved thus, or may be solved as a whole, which, if GAUSS' method be followed, can be done without undue labour, as the coefficients of the various terms remain small whole numbers till near the end of the resolution.

			Residual error in bridge-wire units.
D - E	- H - J - K - L	= n_1	- 0.0158
D	- F - G - H - J - K - L	= n_2	+ 0.0022
D - E	- G	= n_3	+ 0.0136
E - F - G		= n_4	+ 0.0087
F - G - H - J - K - L		= n_5	+ 0.0000
G - H - J - K	- M	= n_6	+ 0.0071
H - J	- L	= n_7	+ 0.0024
H	- K - L - M - N	= n_8	- 0.0024
J - K - L		= n_9	+ 0.0024
K - L - M - N		= n_{10}	+ 0.0008
L - M - N		= n_{11}	- 0.0110
M - N		= n_{12}	+ 0.0002
N		= n_{13}	- 0.0132

It will be observed that the largest residual is only 0.0158 mean bridge-wire unit, or about 0.00003 ohm, showing that when all the contacts are kept clean the uncertainties due to variability of the contact-resistance are exceedingly small, and that the form of contact-maker employed is extremely constant in its action.

The largest residual observed in any standardization was 0.00008 ohm, and the average was about a quarter of this amount.

XIX. *Changes in the Resistance-Coils.*

In order to give an idea of the magnitude of the changes which took place during the work, we give in the following table the values obtained for the wire coils in the first and last standardizations expressed in mean bridge-wire units. In the fifth column is shown the change which took place in each coil, not taking into account the variation of unit. The figures were obtained by dividing the values in the fourth column for the several coils by the corresponding values in the third. The absolute magnitude of the changes cannot be deduced with certainty, but from other experiments made by one of us with manganine wires it seemed probable that the total change in any coil is in reality a combination of two distinct effects, the one being a change in the specific resistance of the wire throughout its entire length, and the other an effect confined to a small length at each end, which was very strongly heated during the operation of hard-soldering it to the copper tags.

Examination of the appended results shows that the change in the value of the lower coils is relatively much greater than in the case of the higher ones. This is in accordance with what we should expect, if the statement above were true, and both changes tended in the same direction.

	Nominal value in ohms.	Value No. 1.	Value No. 4.	$\frac{4}{1}$	
A	40	18761.17	18763.71	1.00014	Wound on glass tubes.
B	20	9391.12	9393.25	1.00023	
C	10	4697.67	4698.80	1.00024	
D	4	1872.63	1874.01	1.00074	
E	3	1406.88	1407.39	1.00036	
F	2	939.276	939.562	1.00030	Hanging free in air.
G	1	462.770	463.047	1.00060	
H	.4	192.719	192.880	1.00083	
J	.3	146.367	146.610	1.00166	
K	.2	99.444	99.616	1.00172	
L	.1	48.498	48.627	1.00265	

XX. Determination of the Temperature-Coefficient of the Coils.

Preliminary determinations had shown that the temperature-coefficient of the wire used for the coils was extremely small, and had we been able to keep the box-temperature anywhere near constant we would hardly have needed to take it into account at all. As, however, considerable variations of the temperature of the room were inevitable, as previously explained, a method had to be devised to determine the coefficient with considerable accuracy. It had been previously found by one of us that the annealing process, to which the wire must be subjected to minimise subsequent time-changes in its resistance, has an appreciable effect on the temperature coefficient of the wire. In nearly all the specimens examined, the point where the characteristic change in sign of the temperature-coefficient takes place was displaced so as to occur at a lower temperature.

In view of uncertainties in the method of subjecting a sample of the wire to treatment *exactly* similar to what the coils themselves had received, and determining the coefficient of this piece—the process usually followed—we attempted to measure directly the actual coefficient of the coils themselves *in situ*.

To do this we first tried a method consisting in the determination of the apparent value in box-units of a resistance kept at constant temperature, while the box-temperature was varied between that of the tap-water circulated through the outer tank and a maximum of about 35°. During these determinations every care was taken that the temperature of the coils as registered really represented their mean temperature at the time. Without going into details as to how this was attained by keeping up a continuous circulation of hot or cold water in the outer tank, and other precautions, we may say that the results of the measurements made were somewhat unsatisfactory, and the reason of this was traced to a curious and, we believe, not previously observed behaviour of the alloy in *not taking up instantaneously the resistance corresponding to a new temperature to which it may be subjected, especially when*

cooling. We found that if the results of the separate determinations of the value of a constant outside resistance made with a series of steady box-temperatures with temperature *rising* be plotted, along with those of a series similar in every respect but with the temperature *falling*, the two do not overlap but form a loop. After a determination commenced at about 15° , during which the resistance-box was heated to 31° and allowed to cool, the whole temperature change occupying about nine hours, the coils did not return to their original resistance at 15° till they had been at this temperature about three days. We satisfied ourselves that this was due to a real lag in *resistance* and not in the indications of the box thermometers. The whole hysteresis effect is, however, small, and is quite imperceptible if the temperature changes are very slow, like the variations of laboratory temperature to which the box was ordinarily subjected. We may say that the temperature coefficient of the sample with which we observed the effect is rather abnormally small even for manganine, and that we had not time to see if the same effect could be observed with other specimens.

Although from the values thus obtained we might have deduced the temperature coefficient, using only the determinations made after a rise of temperature, we considered it advisable to make some fresh experiments, using a modification of the same method. During the first series of observations with thermometer K.8, a considerable number of zeros had been taken during a period when the box-temperature differed markedly from day to day. The thermometer had meanwhile never been disconnected from the box; the contacts remained in the same condition throughout, and we have no reason to believe that any secular change occurred in the leads or thermometer wire during the experiments. These experiments, during which the box temperatures ranged from $6^{\circ}60$ to $19^{\circ}65$, were accordingly utilised to calculate the temperature-coefficients of the coils, and from them a formula was obtained by least squares for the change of resistance of the box-coils with temperature.

Choosing as a standard temperature 15° , a table was calculated giving the coefficients by which the nominal box-resistances must be multiplied to give the true resistances. This multiplier is alluded to subsequently as the "factor" in the example of the method of calculating an experiment given later. The following numbers extracted from the table, show the magnitude of the coefficient in question:—

Temp.	Factor.	Temp.	Factor.
5°	$1 - \cdot 0000602$	13°	$1 - \cdot 0000169$
6	- 569	14	- 087
7	- 530	15	$1 + \cdot 0000000$
8	- 485	16	+ 093
9	- 434	17	+ 193
10	- 377	18	+ 299
11	- 314	19	+ 410
12	- 244	20	+ 528

The coils used for this experiment were those lettered C and E, 10 and 3 ohms respectively, which may be taken as fairly representative. They enter into nearly all the comparisons with K.8.

It may be pointed out here that the influence of the variations of box-temperature on the results is largely eliminated in the experiments, as the fundamental points of the platinum thermometers were determined before, during, and after each series of experiments, and if a wrong value were taken for the coefficient to reduce all these to standard temperature, the errors committed would practically compensate one another.

We may mention here that the coefficients deduced by the method described above show a satisfactory agreement with those found from the *ascending* series of observations made by the first method, although the coils used in the two cases were not exactly the same.

XXI. FIXED POINTS OF THE PLATINUM THERMOMETERS.

Before the commencement of each series of platinum thermometer comparisons a set of determinations of the zero and steam-points, generally about six in number, was always made; frequently check determinations of these points, especially of the zero, were interspersed between the comparisons themselves, thus giving an indication of the exact time when changes, if any, really took place. The zeros were taken in an apparatus similar in all respects to that described later in treating of the gas thermometer.

A few of the first steam-points were taken in an early form of the boiling-point apparatus usually employed at the Breteuil Laboratory, originally designed for mercury thermometers. During a long series of preliminary control comparisons between the platinum and gas thermometer at 100° we found, however, a very small but systematic discrepancy in the results, which disappeared when the steam-points of both thermometers were taken in the same apparatus. We therefore arranged that the same steam-point apparatus should be used by both of us in all the subsequent experiments.

The apparatus for the determination of the boiling-point of sulphur, and the special experiments made with it, are described later on p. 97.

XXII. HEATING OF THE THERMOMETER WIRE BY THE CURRENT.

It is manifest that however small the current employed in the thermometers may be, it must needs heat them to some extent. Although the amount of this heating would be difficult to calculate, yet we thought it advisable to make a few experiments with a view to determine it, and at the same time to get some data from which we

might be able to fix upon the best magnitude of the current to be employed for the thermometric measurements.

For this purpose we made a number of determinations of the apparent resistance of thermometer K.8 in ice using different battery-currents.

For these a curve was constructed showing the increase in apparent resistance of the wire with increasing energy absorbed in the coil, and a value calculated for what the resistance would be, if the current through it (and, consequently, the heating effect) were vanishingly small. Our measurements conclusively showed that, within the limits of accurate experiment, the heating effect was directly proportional to the watts in the wire, and that the heating per milliwatt for K.8 was about $0^{\circ}\cdot006$.

In some of the earlier experiments, made before the heating effect was investigated, we employed a total resistance in the battery circuit of 150 ohms for measurements at 0° ; the heating due to the current in this case being $0^{\circ}\cdot024$. For all the subsequent experiments, however, by increasing the external resistance the heating was diminished to $0^{\circ}\cdot014$ in ice.

Although we only made direct determinations of the magnitude of the heating effect at 0° , we have assumed, in the absence of further data, that for a thermometer coil the heating due to a given amount of energy expended in it is the same at all temperatures. As this is only approximate, some of our results may subsequently require small modifications; but the value we give later for the boiling-point of sulphur would not be affected, as it is expressed on the scale of the gas thermometer, the platinum thermometers being only used as an intermediary.

We calculated a table for each of the principal platinum thermometers, giving the resistance to be inserted in the external circuit for different temperatures.* In the example of a platinum temperature calculation given later, this number is referred to as the battery resistance "B.R. = 317 ohms."

XXIII. DETERMINATION OF THE CENTRE OF THE BRIDGE.

The index-error of the scale was determined from time to time during the work by reducing the resistances between C_1C_2 and P_1P_2 (fig. 1, p. 41) to zero, fixing all the contact pieces firmly in position, and determining the point of balance of the bridge. Should this not fall strictly at the centre of the scale, a correction for "bridge-centre" is applied in each resistance measurement.

* It was afterwards found that the formula used to calculate the table referred to was not strictly correct, but made the external resistance at high temperatures greater than it should have been. As, however, the total current heating at 0° was only $0^{\circ}\cdot014$, and less than this at higher temperatures, the correction to be applied to the results, on account of the adoption of wrong external resistances, is probably well within the limits of experimental error, especially seeing that the error introduced is already partly compensated by its effect on the fundamental intervals as well as on the platinum temperatures found.

[Paragraph added December 1, 1899.—The measurements by which we attempted to determine the scale of the platinum thermometers may be divided into four groups, in which different instruments and means of heating were employed, and in which the precision varied from group to group.

These are—

- (1) Comparisons in water between 0° and 50° of platinum thermometers K.8 and K.9 with the four principal mercury standards of the Bureau.
- (2) Comparisons of K.8 and K.9 in an oil bath at temperatures between 80° and 200° , with a constant volume nitrogen thermometer, the initial pressure of the gas being 793 millims. of mercury.
- (3) Comparisons of thermometers K.8 and K.9 between 250° and 460° in a bath formed of a mixture of nitrates of potash and soda, with the nitrogen thermometer, the initial pressure being 529 millims.
- (4) Comparison of thermometer K.2 with the same nitrogen thermometer in the same bath between the temperatures 424° and 586° , the initial pressure being 392 millims.

As the sensibility of the gas thermometer varies according to the initial pressure, it is evident that the same precision cannot be attained in the different series. The construction of our instrument was such that the highest measurable pressure was about 1400 millims.]

XXIV. GENERAL CONSIDERATIONS ON THE GAS THERMOMETER.

In accordance with the decision of the International Committee of Weights and Measures,* the provisionally accepted normal scale of temperature is that of the constant-volume hydrogen thermometer. The employment of hydrogen for our work seemed therefore advisable, and before proceeding to the actual comparisons, we made a number of trials of the hydrogen thermometer between 100° and 200° . Up to temperatures about 180° these experiments gave fairly good results, but we noticed that prolonged heating above 180° was generally followed by a diminution of the gas contained in the thermometer reservoir. This diminution, though small, being regularly reproduced after each prolonged heating, might become serious at higher temperatures. Some special measurements, made on a known quantity of hydrogen enclosed in a capillary of "verre dur" of 1 square millim. cross section, and exposed

* The resolution fixing this was passed by the International Committee on October 15, 1887, and is as follows :—

"That the International Committee of Weights and Measures adopt as the Normal Thermometric Scale for the International Service of Weights and Measures, the centigrade scale of the Hydrogen Thermometer having as fixed points the temperature of melting ice (0°), and that of the vapour of distilled water in ebullition (100°) under the normal atmospheric pressure; the hydrogen being taken under the manometric initial pressure of one metre of mercury, *i.e.*, at $\frac{1000}{760} = 1.3158$ of the atmospheric pressure."

repeatedly to temperatures varying from 200° to 250° , showed that the volume of the gas regularly diminished.

It therefore seems evident from these experiments that the walls of "verre dur" absorb a minute quantity of hydrogen.

It appears probable that this absorption is due to the reduction of sulphates contained in the glass. The employment of lead-glass as the material for the reservoir instead of "verre dur" would probably give rise to still more serious effects on account of the reduction of the salts of lead.

To avoid in the measurement of temperature the uncertainties caused by the variations of the gaseous mass, of which we have just spoken, and which might affect not only its quantity but its composition, we have substituted *nitrogen* for hydrogen. The nitrogen scale certainly diverges a few thousandths of a degree from the hydrogen scale in the interval 0° to 100° . Its departure from the normal scale at high temperatures is likely to be small and can always be corrected subsequently, when the necessary data have been collected.

The initial pressures of the *nitrogen* gas thermometer show no diminution, but rather a slight increase, which is explained by the contraction of the glass due to the annealing.

XXV. COMPARISONS OF THE PLATINUM THERMOMETERS K.8 AND K.9 WITH THE MERCURY STANDARDS.

The direct comparison of the platinum thermometers with the large normal hydrogen thermometer between 0° and 100° would have necessitated such an enormous amount of work, without offering any special advantage, that we decided not to employ this instrument, but to take instead the four primary mercury standards of the Bureau, Tonnelot thermometers Nos. 4428, 4429, 4430, and 4431, whose corrections to the hydrogen-scale have been previously determined with all possible precautions by one of us. An account of this work is given in vol. 6, 'Trav. et Mém. du Bureau International.'

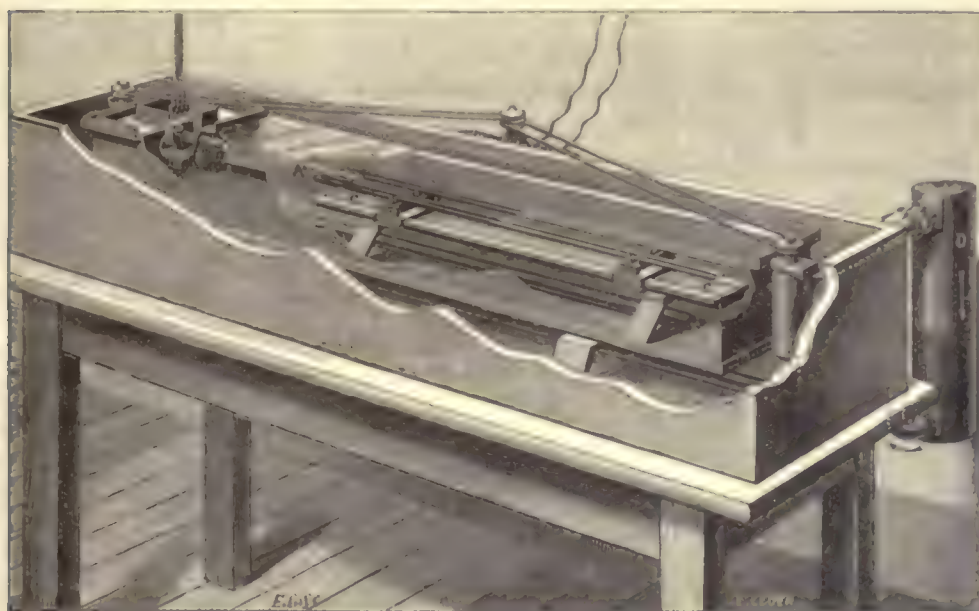
The comparisons between these mercury standards and the platinum thermometers were made in an apparatus constructed originally for the comparison of mercury thermometers with each other, which was modified and considerably improved for the purpose of this research. This apparatus is shown in fig. 11.

It consists of two concentric, rectangular, copper troughs; the outer one, which is protected by an oak case, having a capacity of about 70 litres. This trough communicates by a side tube with a small vertical copper vessel, well protected against radiation, which can be heated by a large gas burner. A screw stirrer, worked by a small motor, drives through the heater a rapid current of water, which is taken in at the opposite end of the trough by a horizontal tube resting on the bottom, and circulates as shown by the arrows in the figure.

The interior trough, which is 112 centims. long, 17 centims. wide, and 14 centims. deep, is provided at one end with a system of screw blades for stirring. Resting upon its bottom is the metal framework on which the thermometers are arranged. This thermometer support is so contrived that all the thermometers can, without risk of straining them, be simultaneously clamped parallel to one another, and in the same horizontal plane.

During the comparisons the platinum thermometer was fixed horizontally, with its spiral in the same plane as the mercury thermometers, and close to them. To prevent the water from penetrating to the portions of it which were exposed, the head

Fig. 11.



Horizontal Bath for Comparisons in Water.

A, stem, and *e*, head, of platinum thermometer; *l*, brass box surrounding the head of platinum thermometer; *D*, heater for water in outer tank; *c*, plate of milk glass.

was placed in a square brass box open above and provided with a side tube, through which the greater part of the length of the thermometer stem projected, the joint being made by an india-rubber stopper.

The internal tank is provided with a rim, on which rests a piece of plate glass 8 millims. thick, covering the whole surface of the water, with which it is just in contact.

By this arrangement the cooling by evaporation is almost entirely prevented, and the attainment of a very constant temperature much facilitated. When operating at temperatures below that of the room, it is advisable to cover the glass with a thin layer of water, in order to avoid the deposition of dew upon it.

The readings of the mercury thermometers are made by means of a small vertical reading telescope sliding on the glass plate, and can be made while the stirrer is at work. The space around the inner tank is closed above by a metal lid, pierced with the necessary openings for the axes of the stirrers.

Observations with Thermometer K.8.

The thermometer K.8 was compared under these conditions with the four standards at temperatures between 0° and 50° . These experiments are numbered 4 to 17 in the summary of results for K.8 at the end. To avoid the errors of parallax on the mercury thermometers, ten readings were made with the divisions upwards and ten with the thermometers turned through 180° . After each series the zeros of the mercury thermometers were observed in the usual manner with a micrometer telescope.

Three other observations at higher temperatures (numbered 18 to 20 in the table) were made with the same thermometers in another apparatus, described later when treating of the gas thermometer. In the three experiments all the instruments were used in the vertical position.

Care was taken to have only a very small emergent column in each case. The bath was filled with oil, and was heated by the vapour of ethyl alcohol boiling under various pressures.

We also made three measurements below 0° in an apparatus specially constructed for experiments at low temperatures, which has been described in the 'Procès-verbaux des Séances du Comité International,' 1891, page 33. The thermometers plunge into a bath of alcohol cooled by the evaporation of liquid methyl chloride, and stirred continuously by a suitable mechanism. The two mercury standards, Tonnelot thermometers Nos. 11,165 and 11,166, which were employed for these observations, have been studied at the Bureau, and compared directly with the hydrogen thermometer under the same conditions.

The series we made consists of three experiments numbered 1 to 3 in the Summary.

Observations with Thermometer K.9.

The later series of comparisons of thermometer K.9 with the mercury standards was made under precisely similar conditions to those described above for K.8, but the number of different points in this case was not so great; each experiment consisted of only ten observations instead of twenty as before. The experiments between 0° and 50° are numbered 1 to 6 in the table.

XXVI. DESCRIPTION OF THE GAS THERMOMETER.

The gas thermometer we employed for our researches is similar to the instrument previously described by one of us* and is shown in fig. 12.

It is a constant-volume thermometer arranged so as to permit the determination of the total pressure of the gas contained in the thermometric reservoir *by a single reading*. The simplification thus introduced into the measurements permits rapid observations without sensibly diminishing the precision, which is limited more by the conditions of uniformity of the baths and other heating arrangements employed than by reading errors.

The apparatus constituting the gas thermometer is installed on a foundation of concrete about 1 cubic metre in volume abutting against one of the massive walls of the laboratory. On this foundation on the left hand rests a rectangular stone pillar, with slate top, carrying the manometric apparatus, while the heating baths on the right are supported on the same foundation at floor level, this however not being shown in fig. 12. The manometric apparatus is protected from heating by a large paper screen which extends upward right to the ceiling, and which is pierced with the holes necessary to admit the passage of the various connecting portions.

(a) *Thermometric Reservoir.*

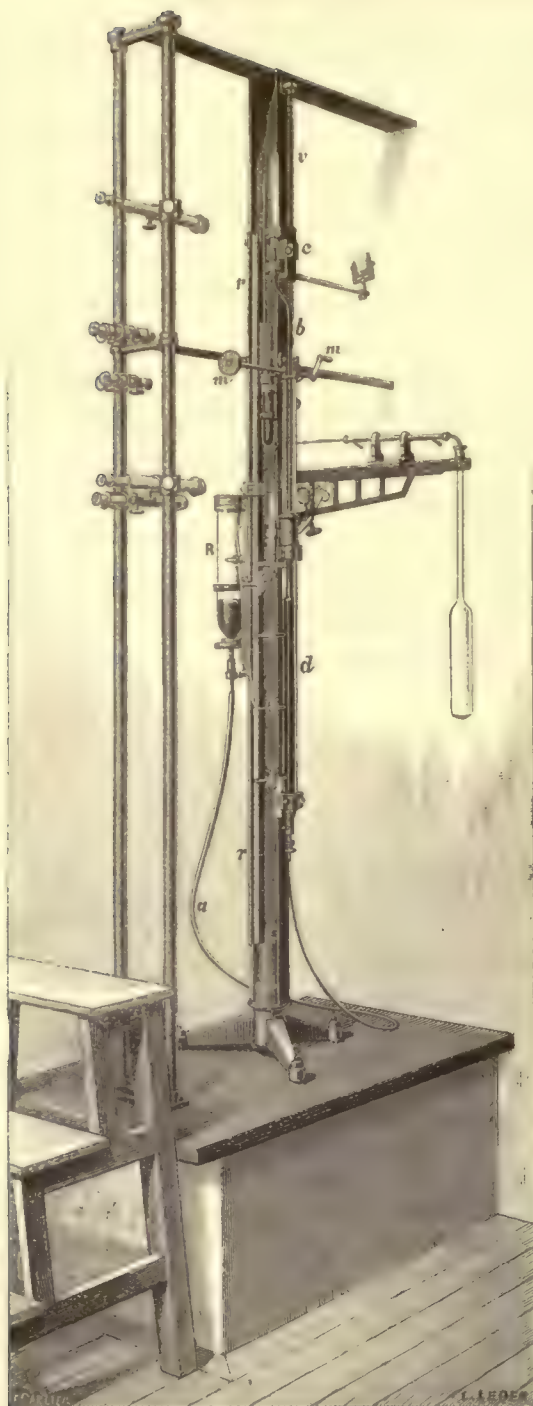
For the first part of the experiments we employed a cylindrical reservoir of hard glass drawn from a tube 36 millims. external diameter and 1.5 millims. thick.

This tube, closed at one extremity, was fused at the other to a capillary tube of the same glass, having a bore of 0.53 millim. and 90 centims. long. Fig. 12 shows the thermometric reservoir mounted for the experiments, its axis being in the vertical position, which we find the most convenient for the introduction of the reservoir into the various baths employed. The outer bend of the tube carrying the reservoir is supported by a light frame from the iron girder carrying the manometer, and slides vertically along this through a considerable distance.

The porcelain reservoir employed for work at high temperatures was obtained from the Royal Porcelain Factory at Berlin. It is cylindrical in shape and is 36 millims. external diameter and 20 centims. long. The reservoir has a neck 28 centims. in length and 11 millims. exterior diameter. It is pierced with a hole of 2 millims. diameter, into which just passes the platinum capillary uniting the reservoir to the manometer. The joining of the platinum tube to the neck of the manometer is a matter of some difficulty, since it is of great importance that this joint should be absolutely gas-tight. We finally adopted the following disposition which has answered well. On the platinum tube which enters to a length of 11 centims. into the neck of the reservoir, a brass washer is soldered which fits exactly to the flat end of the

* 'Trav. et Mém. du Bureau International,' vol. 6, p. 28.

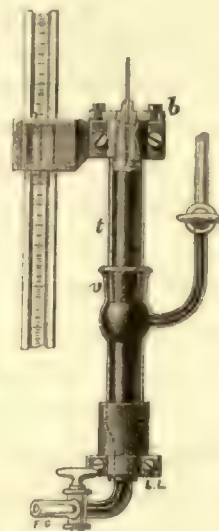
Fig. 12

*Sketch of Gas Thermometer.*

The reservoir is shown raised above its natural position in the comparison bath, and the screens are all removed.

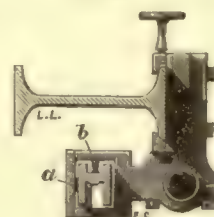
R, mercury reservoir; *a*, steel connecting tube; *r, r*, scale; *c* and *v*, slide and worm gear holding the barometer and scale; *m, m*, handles for adjustment of position of barometer and scale.

Fig. 13.

*Detail of Manometer-point.*

t, glass tube optically ground inside and out; *b*, brass collar, holding the cylindrical stopper of nickel-steel; *v*, ground joint.

Fig. 14.



Section of slide carrying the manometer and scale.

Fig. 15.



Zero apparatus.

neck. This washer is tightly held in place by a brass clamp, which screws on to a collar made in halves and fixed to the narrow part of the neck by a cement, which is a little less fusible than that employed for the joint proper.

(b) *Barometer and Manometer.*

The manometric apparatus is mounted on a vertical iron girder, 2 metres high and of H-shaped cross-section, solidly bolted by three diverging iron feet to the massive pillar previously described. The external faces of the girder are planed up as true as possible over their entire length, and on them slide supports for the manometric tubes, the barometer, and mercury reservoir. To increase the stability of the whole, the top of the iron column is fixed to the wall by a transverse piece, which also serves to support two brass tubes on which slide the observing telescopes.

The barometer consists in its upper part of a tube of 15 millims. internal diameter. A point of black glass is fixed axially in the interior of this tube by fusion. This is referred to subsequently as the *barometer-point*. Below the barometric chamber the tube has a double bend, which brings the lower part of the tube 4 centims. to the right of the upper portion.

The barometer tube is firmly fixed above to a carriage, *c*, which can be displaced vertically by the movement of a screw 60 centims. in length, working in bearings above and below, and engaging by bevel gearing with a horizontal shaft projecting forwards. By turning the small handle *m* the barometer can be raised or lowered at will.

The piece which maintains the barometer tube on its support also carries suspended between two points by one of its extremities a graduated brass scale 1.5 metres long, whose axis is at a distance of 48 millims. from the barometer point. This scale shares all the movements of the barometer carriage, and the glass point may be assumed to have an invariable position with reference to the neighbouring divisions of the scale.

The lower end of the barometer is immersed under mercury in a tube of 90 centims. in length and 25 millims. in diameter, which serves as its reservoir; this tube can be fixed at different levels on the manometer support.

Projecting from the front of this tube are four stop-cocks at intervals of 15 centims., serving to establish communication between the barometer and manometer at any height.

The open branch of the barometer communicates below by means of a long steel tube, *a*, with a reservoir, *R*, of large capacity filled with mercury, which can be displaced vertically either rapidly by hand or slowly by a micrometer screw.

(c) *Manometer.*

The closed branch of the manometer, the details of which are shown in the fig. 13, is composed of a rather thick-walled flint glass tube 16 millims. internal diameter,

which has been optically worked inside and out, in order to render it perfectly cylindrical; the freedom from longitudinal striæ thus obtained gives great sharpness to the images obtained through it. The upper end is closed by a stopper of glass or metal, pierced with a fine hole. Into this stopper is fastened the end of the capillary tube fused to the thermometric reservoir. The stopper, which is ground perfectly cylindrical, enters the tube, which it fits closely, for a length of 25 millims., and is fixed in position by a very thin layer of Canada balsam, thus forming a perfect joint.

The lower part of the stopper is plane and well polished, and carries at its centre a very fine steel point 0.5 millim. long, which serves as an index mark to which the mercury may be accurately adjusted. To avoid all displacement of the stopper and tube in their support, a brass collar is fixed in a groove ground in the stopper, and this is firmly screwed to the iron support by the clamp *b*. The piece of bronze carrying the manometer tube also serves to maintain the position of the lower end of the scale, and to carry the vernier, whose zero thus occupies an invariable position with regard to the steel point in the manometer tube. The closed limb of the manometer is so arranged on its support that its axis is in the same vertical line as the point in the upper chamber of the barometer. The scale remains vertical for all positions of the sliding supports of the barometer and manometer. These conditions being fulfilled, it is evident that if the distance between the point in the closed branch and the zero of the vernier is once for all known, a single reading of the scale, corrected for the "index error," which is defined later, suffices to give the difference of level between the two points.

The closed branch of the manometer fits below into a glass T-piece, the horizontal limb of which communicates with a system of tubes serving for the exhaustion and filling of the reservoir. The lower end of this glass tube is bent horizontally forwards, and communicates by a tap with one of the four taps on the open branch of the manometer.

(d) *Measurements of Pressures.*

The disposition of the manometric apparatus permits, as has just been seen, the measurement at any moment of the distance between the two points in the barometer and the closed branch. The communication between the columns of mercury filling the manometer and the barometer reservoir being established, the pressure exerted by the gas on the mercury in the closed branch is balanced by increasing or diminishing the height of the mercury in the open branch, which is effected by raising or lowering the auxiliary reservoir placed on the left. The barometer tube is simultaneously displaced, in order to keep the mercury in the neighbourhood of the point in the barometric chamber. The equilibrium sought is attained when the mercury just reaches at the same time the points in the closed branch and in the barometer chamber. The observation of this adjustment of the mercury is made by means of two small telescopes magnifying about 36 times, sliding vertically on a brass

tube and placed at a distance of 38 centims. from the manometer. A second tube serves to support three other small telescopes, for the observation of the scale-vernier, and two auxiliary mercury thermometers, which are placed close to the mercurial columns to indicate their temperature.

During the measurements the observer is at a distance of about 50 centims. from the apparatus; his influence on the temperature of the mercurial columns is thus considerable, as is also that of the various heating baths, and by reason of the great expansion of mercury, this heating probably constitutes one of the principal sources of error in the experiments. To diminish as far as possible the radiation from the comparison-bath, a double walled metallic screen, in which a current of water circulated, was interposed between it and the manometer.

(e) *Divided Scale.*

The divided scale used was constructed by the Société G  n  voise, and has served for previous work with the gas thermometer. Its length is 1.5 metres, and its cross-section is in the form of an H. This H-form is not well adapted for use with a vernier. It would be better to adopt a form allowing the surfaces carrying the divisions of the scale and vernier to be in the same plane. In this scale the divisions are on a plate of silver let into the median transverse face, very near the plane of the neutral fibres.

Fig. 14 shows in horizontal projection the disposition of the pieces which support the scale and attach it to the barometer, and fig. 13 the pieces which hold the vernier on the support of the manometer tube, and which ensure contact between the scale and the vernier. The method of suspension of the scale permits it to turn about two axes perpendicular to its length. In the two directions of free movement two springs gently press the scale against the vernier.

Two thermometers placed at equal distances from the points in the barometer and manometer tubes, the one on a fixed support, the other on an attachment to the barometer, serve to indicate the temperatures of the mercurial columns and of the scale. Each of these thermometers is placed in a test-tube filled with mercury, of the same diameter as the neighbouring portion of the manometer tubes. This symmetrical arrangement of the thermometers with regard to the ends of the mercury columns whose temperature is to be measured considerably simplifies the calculation of the mean temperature of the manometer.

XXVII. ZERO APPARATUS.

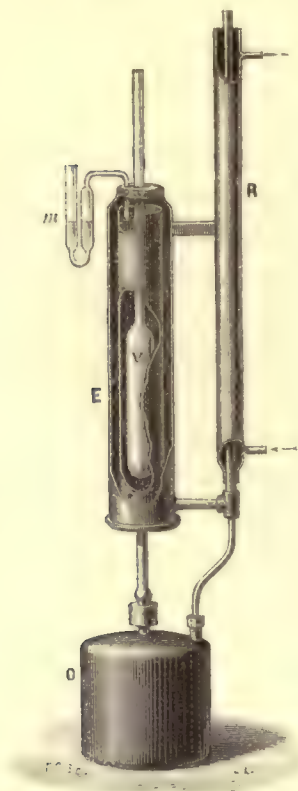
A glass bell-jar supported on an iron tripod and surrounded by several layers of felt serves as the receiver. The ice, finely divided and saturated with pure water, is pressed around the reservoir of the thermometer, the emergent stem being held by a

clamp fixed on the support of the bell-jar. The apparatus, filled with ice and protected by a cover of thick flannel, can be left three or four hours without the least perceptible change of temperature in the central part occupied by the reservoir.

XXVIII. STEAM-POINT APPARATUS.

The 100-point apparatus, shown in fig. 16, is composed of a small boiler of 3 litres capacity, communicating by a lead tube with a double walled vertical vessel, into

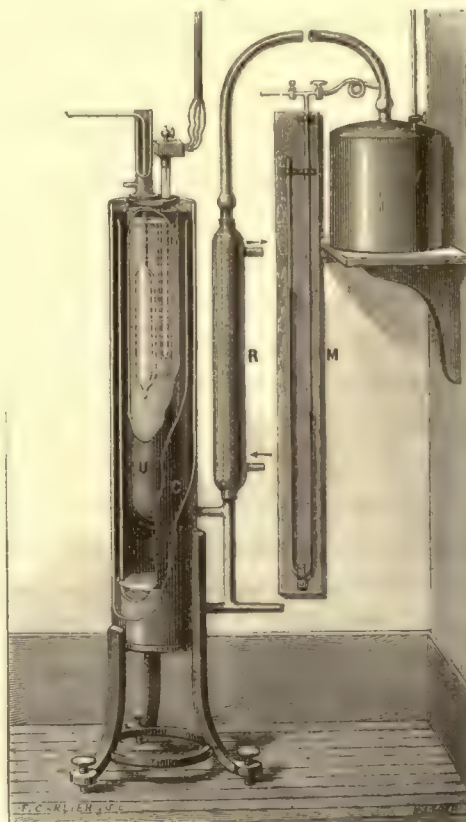
Fig. 16.



Steam-point apparatus.

- V, reservoir of gas thermometer.
- O, copper boiler.
- E, double-walled cylinder.
- R, condenser.
- m, water manometer.

Fig. 17.



Oil-bath for comparisons to 200°.

- NOTE.—The stirring arrangements are not shown.
- U, copper oil vessel.
 - R, condenser.
 - V, air reservoir.
 - M, manometer.
 - C, wall of vapour bath cut away to show interior.

which the thermometer reservoir can be introduced from above. The vapour developed in the boiler first passes up the inner tube of the steam bath, then descends by the exterior annular space, finally arriving at the condenser, whence it

returns to the boiler by a tube plunging below the water-level. All the communication tubes between the different parts are wide, and arranged so as to avoid the possibility of their becoming choked by the condensation of water in them. The excess of the interior pressure over that outside can be measured by a small water-manometer introduced into the cork.

XXIX. COMPARISON-BATH FOR RANGE 80° TO 200°.

The disposition of this apparatus, indicated in fig. 17, is the result of a long series of experiments, the aim of which was to obtain a bath sufficiently uniform in temperature to be employed for the accurate comparison of mercury thermometers with the gas thermometer over the range mentioned. It fulfils satisfactorily the principal requirements of an apparatus of this kind, viz. :—

- (1) Uniformity of temperature throughout a space of large dimensions.
- (2) Rapid re-establishment of a steady state after the pressure in the boiler has been altered.
- (3) Employment of a small number of inexpensive liquids easily obtained in a state of sufficient purity.

The boiler consists of a cylindrical vessel of planished copper 2 millims. in thickness ; it has a diameter of 17 centims. and a height of 82 centims. A bell-shaped vessel of the same material is soldered by its rim concentrically into the interior of the cylinder. This inner vessel is filled with a heavy petroleum oil, in which the reservoirs of the thermometers to be compared are directly immersed.

The stirring is effected by a vertical stirrer (not shown in the figure), the stems of which emerging from the bath are protected against cooling by glass tubes. The annular space between the two vessels serves for the circulation of the vapour, and to increase the uniformity of this circulation the space is divided into two approximately equal parts by the introduction of a thin tube of copper open at both ends, and resting on the bottom of the cylinder. The vapour given off by the boiling liquid, which fills the lower part of the outer vessel, rises first in the interior space in contact with the walls of the oil-bath, then descends by the exterior, again ascending into the condenser placed at one side, whence it passes in the state of liquid back to the boiler by a lateral tube. The reversed condenser is in communication by a wide tube with a large copper reservoir in which the pressure can be varied at will, or kept constant, thus changing the temperature of ebullition by a considerable amount ; by using only three liquids any temperature between 80° and 200° can be quickly attained and kept extremely constant for any length of time, provided only that the joints in the whole apparatus remain perfectly tight. A mercury manometer indicates the pressure of the vapour. The bath is covered with several layers of asbestos-card to avoid losses by radiation and their effects on the temperature of the room.

XXX. PRELIMINARY DETERMINATIONS.

(a) *Measurement of the Capacity of the Thermometric Reservoir.*

Before proceeding to the measurement of the capacity of the thermometric reservoir, we considered it advisable to subject it to a prolonged annealing at the temperature of the boiling-point of sulphur. After thirteen hours' heating we obtained for its capacity at 0°

$$V_0 = 159.670 \text{ cub. centims.},$$

and after a second exposure of eleven hours we found

$$V_0 = 159.642 \text{ cub. centims.}$$

This value was a little modified during the operation of mounting the thermometer, as a short piece of the connecting capillary had to be suppressed. Allowing for this we found for the first part of the experiments the value

$$V_0 = 159.629 \text{ cub. centims.}$$

(b) *Coefficient of Dilatation of Hard Glass.*

The dilatation of "verre dur" was not measured directly on the thermometric reservoir itself, but on a tube of 1 metre length drawn from the same melting; its linear dilatation was determined by a long series of experiments at temperatures comprised between 0° and 100° . These experiments have given for the law of cubic dilatation of glass between 0° and 100° the formula

$$V_t = V_0 (1 + 0.000\,021\,801\,t + 0.000\,000\,015\,536\,t^2),$$

whence, for $t = 100^{\circ}$,

$$V_{100} = V_0 (1 + 0.002\,335\,50).$$

During some subsequent experiments on the effect of prolonged heating on glass, we had occasion to control this result by determining the dilatation between 0° and 100° of a "verre dur" vessel drawn from the same tube as the thermometric reservoir. From these observations we found

$$(1) \text{ Before annealing. } \dots \dots V_{100} = V_0 (1 + 0.002\,357\,1),$$

$$(2) \text{ After annealing at } 445^{\circ} \text{ for 81 hours } \dots V_{100} = V_0 (1 + 0.002\,343\,6).$$

These last measurements furnish no indication of the magnitude of the term in t^2 , which alone has any influence on the temperature measurements. We have therefore employed, for all the observations relative to the glass reservoir, the expression with two terms indicated above.

(c) *Determination of the Coefficient of Pressure of the Thermometric Reservoir.*

The capillary tube fused to the thermometric reservoir had, at the commencement, a length of about 250 millims. The volume of this tube was determined by weighing a thread of mercury occupying in it a length of 200 millims.; the weight of mercury contained in 1 millim. of length was found to be 1.69185 gramme. The calibre of the tube was afterwards studied by GAY-LUSSAC's method between the two extreme points 0 and 250. The calibration corrections thus obtained had to be applied in the reduction of the observations on the coefficient of pressure. To measure this coefficient the same method is followed as for the determination of the coefficient of external pressure of mercury thermometers.

The thermometric reservoir is placed in a glass tube filled with water, and closed by a cork pierced with a hole, through which passes the capillary attached to the reservoir. The space between the reservoir and the external tube can, by means of stop-cocks, be put into communication either with the atmosphere, or with a large exhausted vessel. The reservoir itself being filled with water up to a certain scale division, observations are made of the displacements of the meniscus produced by varying the external pressure by nearly an atmosphere.

The observations effected under these conditions gave, after all reductions, the following value for the variation Δv of the volume of the reservoir, which corresponds to a variation of external pressure equal to a millimetre of mercury,

$$\Delta v = 0.006\ 228 \text{ microlitre.}$$

This value of the coefficient of pressure was employed for the calculation of a table giving the variations of volume of the reservoir corresponding to the changes of internal pressure observed in the course of the experiments.

(d) *Determination of the "Dead Space" ("Espace Nuisible").*

The determination of the volume of the space occupied by the gas not exposed to the same temperature as the reservoir presents peculiar difficulties. It is of extreme importance that the limits of this space should be well defined, which, however, cannot be done quite rigorously.

The "dead space" may be divided into two parts: (1) the space occupied by the gas in the closed branch of the manometer between the mercury touching the point and the lower surface of the stopper, and (2) the internal volume of the capillary tube between the plane of the stopper and the part of the tube which penetrates into the heating apparatus. The curvature of the mercury-meniscus in the closed branch is necessarily somewhat variable, and as the diameter of the tube is 16 millims., small

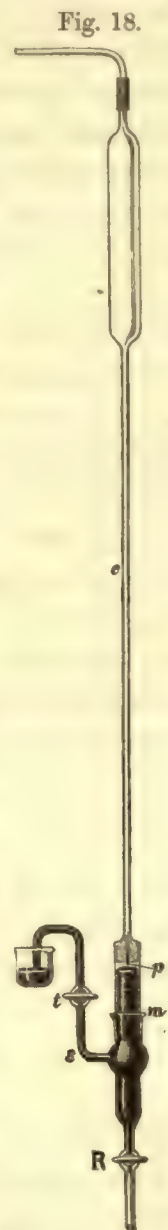
variations in the capillary angle have an appreciable effect on the volume of the gas above the mercury. The extent of the second part on the side of the reservoir is also somewhat uncertain, because of the rapid variation of temperature near its end, but as the capillary tube has only a very small diameter, the influence of this cause of error is not great.

In order to avoid the uncertainty of any hypothesis concerning the capillary angle under the actual circumstances, we attempted to measure the total volume of the "dead space" directly in the following manner.

The capillary tube joining the thermometric reservoir to the manometer being straight, the closed branch of the manometer was fixed on its support in the position it afterwards had to occupy (fig. 18), and the open extremity of the reservoir was connected to the mercury pump. The side tube, *S*, of the manometer terminated in a tube bent downwards, whose lower end was about on a level with the point. The tap, *R*, was placed in communication with the auxiliary mercury reservoir forming part of the gas thermometer. The tube, *m*, was first exhausted, and then filled up with mercury to near the steel point, and the tube, *s*, completely filled; then air was readmitted, and the mercury was adjusted to the point by slightly displacing the reservoir. The taps, *R* and *t*, being then shut, the whole was again exhausted. A small, carefully weighed vessel containing mercury was placed under the tube, *s*, and by opening the tap, *t*, mercury was allowed to enter the manometric tube and fill all the space above the point, rising to the level, *c*, which is at the barometric height above the mercury in the weighed vessel. The volume of the "dead space" could then be deduced from the loss of weight of the small vessel. It should be remarked that the pressure in *m* at the end of the experiment was very nearly the same as at the beginning, and all uncertain corrections were thus avoided. The divergence found between the individual observations given are a fair measure of the inevitable variations of the "dead space" during the experiments.

If the point, *c*, did not coincide exactly with the limits of the "dead space," it would be easy to take account of the difference, the volume of the capillary tube having been previously measured.

The following values for the volume of the "dead space" were obtained by the above method ;—



Determination of the volume of the "dead space."

	cub. centim.
(1)	0·4371
(2)	0·4503
(3)	0·4469
(4)	0·4380
(5)	0·4385
(6)	0·4385
(7)	0·4385

Mean . . . $v = 0·4411$

(e) *Determination of the "Index Error."*

The readings made on the scale by means of the vernier do not represent exactly the difference of level between the points in the barometer and the closed branch of the manometer; this is due to two causes. The first is that the point of the barometer is not at the same level as the division, 0, of the scale. All the scale-readings have, therefore, a correction applied which we will call the correction for "index error," which must be determined by special measurements with a good cathetometer. This correction, which would be constant if the plane surface of the girder on which the barometer slides were absolutely true, varies slightly according to the position of the barometer.

The second cause is that the point in the manometer is not at the same level as the division, 0, of the vernier. This latter correction may, perhaps, be considered constant for a given position of the closed branch of the manometer.

The correction for the "index error" has been determined frequently during the course of the experiments, especially that relating to the lower point, the position of which has been modified several times. The publication of the observations being of no interest, we give simply the values of the constants relating to two positions of the closed branch. From the observations of the 3rd and 4th of May, 1898, the correction relating to the barometer was found to be

$$C_b = - 9·588 \text{ millims.},$$

and the correction relating to the manometer point in the raised position (for observations at 0° and 100°)

$$C_m = + 20·130 \text{ millims.},$$

whence the total correction for "index error" is given by

$$C = C_b + C_m = 10·542 \text{ millims.}$$

In the lower position of the manometer (used in comparisons between 100° and 200°) the total correction had the slightly different value $C = 10·552$ millims.

(f) *Corrections of the Scale and Vernier.*

The corrections of the scale are given in vol. 6 of 'Trav. et Mém. du Bureau International.' We need say here only that the study of this scale by M. ISAACHSEN gives the corrections at each decimetre graduation, except the second, and at all the even centimetres between 500 and 1400.

The vernier is divided into twenty parts, and its total interval (0, 20) corresponds to a length of 18.980 millims. instead of 19 millims. A correction must therefore be applied to the vernier readings, which is proportional to the fraction measured, and whose maximum value is 20 micron.

The measurements made to verify the equidistance of the divisions of the vernier showed that the errors of division attain 10 micron. for certain lines, but by reason of their irregular distribution, and of the repetition of the observations using different parts of the vernier, they have not been taken into account.

XXXI. CALCULATION OF THE TEMPERATURES.

The deduction of the formula employed for the calculation of the temperatures has been given with all necessary details in the memoir already quoted,* therefore we only give here a résumé of the process.

Let V_0 be the volume at 0° of the gas contained in the thermometer reservoir ;

δ the mean coefficient of dilatation of the reservoir between 0° and T° ;

α the coefficient of expansion of the gas at constant volume ;

v the volume of the "dead space" at the standard temperature t° ;

Δv and Δt the variations of volume and temperature of the "dead space" ;

H_0 the initial pressure of the gas corresponding to the temperature 0° of the reservoir and t° of the "dead space" ;

$H_0 + h$ the pressure of the gas at the temperature T° to be determined ; the temperature of the "dead space" being $t + \Delta t$, and its volume $v + \Delta v$;

β , the internal pressure coefficient of the thermometric reservoir.

The total mass of the gas being the same at the temperatures 0 and T , we have

$$\left(V_0 + \frac{v}{1 + \alpha t}\right) H_0 = \left[\frac{V_0(1 + \delta T) + \beta h}{1 + \alpha T} + \frac{v + \Delta v}{1 + \alpha(t + \Delta t)}\right] (H_0 + h).$$

Suppose now that we have applied to the pressures H_0 and $H_0 + h$ the corrections necessary to reduce them to what they would have been had the whole "dead space" been maintained at 0° , and let us call these new pressures H'_0 and $H'_0 + h'$; we have then the simplified formula

$$(V_0 + v) H'_0 = \left[\frac{V_0(1 + \delta T) + \beta h}{1 + \alpha T} + v\right] (H'_0 + h'),$$

* 'Trav. et Mém. du Bureau International,' vol. 6, p. 52,

whence, by certain simplifications, we get finally

$$\alpha T = \frac{H_0' + h'}{H_0'} \left[1 + \delta T + \frac{\beta h}{V_0} \right] + \frac{h'v}{H_0 V_0} (1 + \alpha T) - 1.$$

This formula was used first to calculate the coefficient α between the known temperatures 0° and 100° , the value found being afterwards utilised for the calculation of the temperatures observed in the comparisons.

XXXII. CORRECTIONS RELATING TO THE "DEAD SPACE."

The corrections, which must be applied to the observed pressures, to reduce them to what they would have been had the whole of the "dead space" been at 0° throughout, are easily deduced from the laws of BOYLE and GAY-LUSSAC.

(1) Let us first suppose that the "dead space" is composed of different parts

$$v = v_1 + v_2 + v_3 + \dots$$

whose temperatures are

$$t_1, t_2, t_3, \dots$$

If now we reduce to 0° these gaseous volumes without changing the pressure p to which they are subjected, we have as total variation of volume

$$\Delta v = \frac{v_1}{(1 + \alpha t_1)} + \frac{v_2}{(1 + \alpha t_2)} + \frac{v_3}{(1 + \alpha t_3)} + \dots - v.$$

The temperatures t_1, t_2, t_3, \dots , being generally positive, Δv is negative.

(2) To find the correction sought, it is necessary to transfer from the reservoir, where the temperature is T° , and the pressure p , a quantity of gas occupying at 0° the volume Δv , or what comes to the same thing, the volume of the reservoir V must be increased by a quantity equal to $\Delta v (1 + \alpha T)$. It is evident that this increase in volume involves a variation of pressure

$$\Delta p = p \left(\frac{V}{V + \Delta v (1 + \alpha T)} - 1 \right),$$

which can also be written

$$\Delta p = - \frac{\Delta v}{V} (1 + \alpha T) p,$$

and which represents the correction sought.

For the application of these corrections we constructed two tables. The first gives for every degree the values of

$$v_1 \left(\frac{1}{1 + \alpha t_1} \right), \quad v_2 \left(\frac{1}{1 + \alpha t_2} \right), \quad v_3 \left(\frac{1}{1 + \alpha t_3} \right), \text{ etc.,}$$

and enables the values of Δv to be rapidly calculated.

The second table gives the values of

$$-\frac{\Delta v}{V}(1 + \alpha T)$$

for all the values of T in the comparisons.

XXXIII. FILLING OF THE GAS THERMOMETER.

The nitrogen employed was prepared by the following method; into a solution of 100 grams of potassium bichromate in 900 grams of distilled water were introduced 100 grams of nitrite of soda and 100 grams of nitrate of ammonia. When gently heated, this mixture gives off a very regular stream of nitrogen, which is collected in a large bottle over distilled water. To destroy any oxides of nitrogen which the gas may contain, it was passed through two tubes containing caustic potash, then over copper, heated to dull redness in a combustion tube, and finally through a series of drying tubes containing baryta and phosphoric anhydride. The gas, after remaining a long time over the drying agents, was introduced into the reservoir of the gas thermometer by a series of glass tubes, leading on the one hand to the tap on the manometer-limb and on the other by a side-tube to the mercury pump.

The reservoir was then heated for some time to about 250° , being meanwhile thoroughly exhausted by the mercury pump. Dry nitrogen was then admitted, and the alternate evacuation and filling with gas were repeated several times. Our first definite filling was made on February 2, 1898.

As the comparisons were to extend between the limits 100° and 200° the initial pressure at 0° C. was adjusted to be approximately 800 millims. of mercury, the pressure at 200° corresponding to this being about 1,387 millims. This is nearly the highest pressure which can be measured on the manometer.

XXXIV. DETERMINATION OF THE INITIAL PRESSURE.

It is essential to measure repeatedly the pressure of the gas at the temperature or melting ice, in order to make sure that no leakage takes place at the joints, and to be in a position to take into account the inevitable small variations in capacity which take place when a glass reservoir is employed. As we have previously mentioned, prolonged heating produces a permanent contraction of the glass, therefore we may expect an increase in the initial pressure after the comparisons at high temperatures.

For observation of the initial pressure the zero apparatus, previously described, is used. We give, as an example of a determination, the second series of observations of May 3, with their reductions, in the form adopted throughout the whole of the experiments.

We have taken for the temperature of the "dead space" that indicated by the nearest thermometer, No. 4365.

3RD MAY.

Time.	Vernier readings.	Auxiliary thermometers of the manometer.	
		4365 (low).	4362 (high).
11.0	millims. 784.765 .770 .770 .765	14.960 .950 .930 .940 .970	15.320 .330 .350 .400 .430
11.30	.770		
Mean =	784.768	14.950	15.366
Vernier correction . . . =	+ .015	.054	-.348
Correction for index error . =	+ 10.542		
	795.325	14.896	15.018
Correction for dilatation . =	- 1.934		
" " gravity . . . =	+ 0.263		
" " the scale . . . =	0.026		
Δp =	- 0.114		
Initial pressure =	793.514		
		Mean = 14.957	
		$\Delta v = - 22.9$ microlitres	

All the observations given on the following page have been calculated exactly as in the example quoted, regard being paid to the subsequent modifications in the "index error."

Date.	Initial pressure in millims.	Remarks.
February 3	793.413	From February 4 to 9 six determinations at 100°
" 4	.468	
" 4	.404	
" 5	.456	
" 5	.421	
" 7	.427	
" 8	.395	
" 8	.395	
" 9	.424	
" 9	.406	
April 22	793.516	From April 22 to 27 seven determinations at 100°
" 22	.509	
" 23	.525	
" 23	.498	
" 25	.528	
" 25	.506	
" 27	.511	
" 27	.512	
" 27	.522	
May 2	.543	From May 6 to 10 seven determinations at 100°
" 2	.527	
" 3	.532	
" 3	.514	
May 11	793.557	
" 11	.526	
" 11	.543	
" 12	.536	
" 12	.534	
May 26	793.553	From May 26 to 28 five determinations at 100°
" 26	.544	
" 27	.575	
" 27	.557	
" 27	.548	
" 28	.563	
" 28	.580	
" 29	.569	
" 29	.582	
June 3	793.589	From May 30 to June 2 comparisons with the thermometer K.9
" 3	.574	
" 4	.546	
" 4	.554	

XXXV. DETERMINATIONS OF THE COEFFICIENT OF EXPANSION OF NITROGEN.

The thermometer reservoir and the capillary tube which forms part of it were placed in the boiling-point apparatus described on p. 72.

As regards the parts of the capillary tube included in the "dead space," these

were protected from the heating effect of the boiling-point apparatus by surrounding sleeves of thin copper, traversed by a current of cold water. The temperature was observed by means of a small thermometer placed with its bulb in one of the sleeves.

The temperature of ebullition of the water was deduced from the barometric pressure, observed every 3 minutes, on the auxiliary barometer No. 3 of the Bureau, placed in a neighbouring room, the necessary corrections being of course applied.

The following example, which is one of the observations of May 13, will suffice to illustrate the course of the operations.

DETERMINATION of the 100-point.

Time.	Vernier reading.	Auxiliary thermometers of the manometer.		Reduced barometer in millims.	Excess of pressure of steam in millims. of water.	Temperature of the dead space.
		4365.	4362.			
10.14 A.M.						
17	1072.215	13.835	14.200	751.79	2.8	12.70
21	.220	.830	.200	.79	2.8	.70
25	.210	.820	.185	.79	2.8	.80
29	.210	.820	.190	.74	2.9	.80
32	.210	.825	.210	.72	2.7	.90
10.37	.225	.830	.230	.73	2.8	.90
				.72		
Means	= 1072.215	13.827	14.202	751.75	2.8	12.80
Vernier correction =	+ .004	-.054	-.349	+ .25		
Index error . . . =	+ 10.550					
	1082.769	13.773	13.853	752.00		
Corr. for dilatation =	- 2.432	Mean = 13.813				
" " gravity =	+ .360					
" " scale . =	- .036					
Δp	= .196					
	1080.465					
				T = 99.705		
				Δv = - 21.20 microlitres		

The total volume of the "dead space" being 445.10 cub. millims., the part surrounded by the sleeves, whose volume was 74.76 cub. millims., had the temperature 12°·8 indicated in the last column on the right. For the rest of the "dead space," of volume 366.34 cub. millims., we have adopted the temperature 13°·77 indicated by the auxiliary thermometer No. 4365.

The excess of pressure of the vapour over the barometric pressure is measured by

a small water manometer placed in the cork of the apparatus, and must be transformed to mercury pressure and added to the reduced barometric height. From this total pressure the temperature is deduced by means of the tables published by M. BROCH for the temperatures of ebullition of pure water,* part of which is re-printed in the Appendix to this paper, Table III.

If the small variations of initial pressure during the course of the experiments be taken into account, we obtain, on applying to the observations the formulæ indicated above, the following values for the *coefficient of expansion of nitrogen under constant volume* :—

Date	Coefficient.	Initial pressure in millims. assumed for the calculation.
April 4	0.00367 131	793.421
" 5	244	
" 7	196	
" 8	186	
" 8	134	
" 9	172	
April 22	0.00367 173	793.519
" 22	117	
" 23	148	
" 23	167	
" 25	143	
" 25	126	
" 26	120	
May 6	0.00367 178	793.532
" 6	198	
" 7	195	
" 7	172	
" 8	140	
" 10	145	
" 10	194	
May 26	0.00367 246	793.563
" 26	224	
" 27	227	
" 27	224	
" 28	216	
General mean = 0.00367 180		

The general mean of these four groups of determinations has been employed for the calculation of the temperatures in the series of comparisons made about this time, excepting the series with the thermometer K.9, for which the mean of the last group of observations 0.00367 227 was adopted.

* 'Trav. et. Mém. du Bureau International,' vol. 1 A, p. 46.

XXXVI. COMPARISONS BETWEEN PLATINUM THERMOMETER K.8 AND THE NITROGEN THERMOMETER.

These comparisons were made in the oil-bath previously described (Section XXIX). Fig. 17 shows the arrangement of the two instruments in the comparison-bath. For the first series between 88° and 116° water was employed in the jacket.

Simultaneous observations of the two instruments were made by the authors while an assistant worked the stirrer.

Each comparison at any one temperature consisted of ten observations. To eliminate slight uncertainties due to thermoelectric effects the battery current was always reversed after the first five readings.

The second series of observations, extending from 120° to 160°, was obtained by the ebullition of paraxylene, and the final series up to 190° with aniline.

As we have indicated in the résumé of the zeros on p. 82, the comparisons of K.8 with the nitrogen thermometer may be divided into two groups, the first extending from 88° to 161° (March 23 to April 2) and consisting of twenty-six observations, the second from 89° to 190° (May 14 to 24) and comprising twenty-two observations.

We give as example of a comparison the observations of May 24 at 188°·6.

NITROGEN Thermometer Readings, 24th May.

Time.	Vernier readings.		Auxiliary thermometers of the manometer.	
			4365 (low).	4362 (high).
11.25	millims.			
	1327·260		16°050	17°800
	·570		·060	·800
	·485		·070	·820
	·385		·100	·820
	·370		·100	·845
	·310		·110	·850
	·310		·110	·850
	·300		·120	·900
	·350		·130	·890
11.40	1327·350		16·140	17·880
Mean.	= 1327·369	Total correction .	16·099	17·846
Vernier correction	= + ·007		- ·052	- ·335
Correction for index error .	= + 10·550		16·047	17·511
	1337·926		Mean = 16·779	
Correction for dilatation .	= - 3·647		$\Delta v = - 24·5$	
" " gravity	= + ·444			
" " scale	= - ·048		Nitrogen temperature = 188°588	
Δp	= - ·346			
	1334·329			

PLATINUM Thermometer Readings. Experiment No. 68, 24th May, 1898.

Bridge-centre = — .002 centim. Battery resistance = 317 ohms.

Coils B, F, J = 10488.249. Box temperature = 15°.22.

Factor = 1 + .000 0020.

Readings.

$\alpha.$		$\beta.$	
1	+14.135	6	+14.610
2	+16.875	7	+14.520
3	+16.270	8	+14.900
4	+15.330	9	+14.930
5	+14.810	10	+14.990

Mean bridge-wire reading . . = + 15.137

Bridge-wire correction . . . = — 0.035

Corrected bridge-wire reading = + 15.102

Coils = 10488.249

Bridge-wire reading . . . = + 15.102

Centre correction = + 0.002

Temperature correction . . = + 0.020

Resistance found = 10503.373

Resistance at zero = 6110.805

(R — R₀) = 4392.568

Fundamental interval . . . = 2361.246

Platinum temperature . . . = 186°.027.

In reducing the observations we have taken as the mean of the determinations of initial pressure effected before and after each series the values—

millims.

For the first series . . . H₀ = 793.470 ;
 For the second series . . . H₀ = 793.545.

XXXVII. COMPARISONS WITH THE THERMOMETER K.9.

With the thermometer K.9, which has twice the resistance of K.8, a precisely similar series of comparisons was made. The constants adopted for the calculation of the nitrogen temperatures of this series were :—

Initial pressure = 793.563 millims.

Coefficient α = 0.003 672 27,

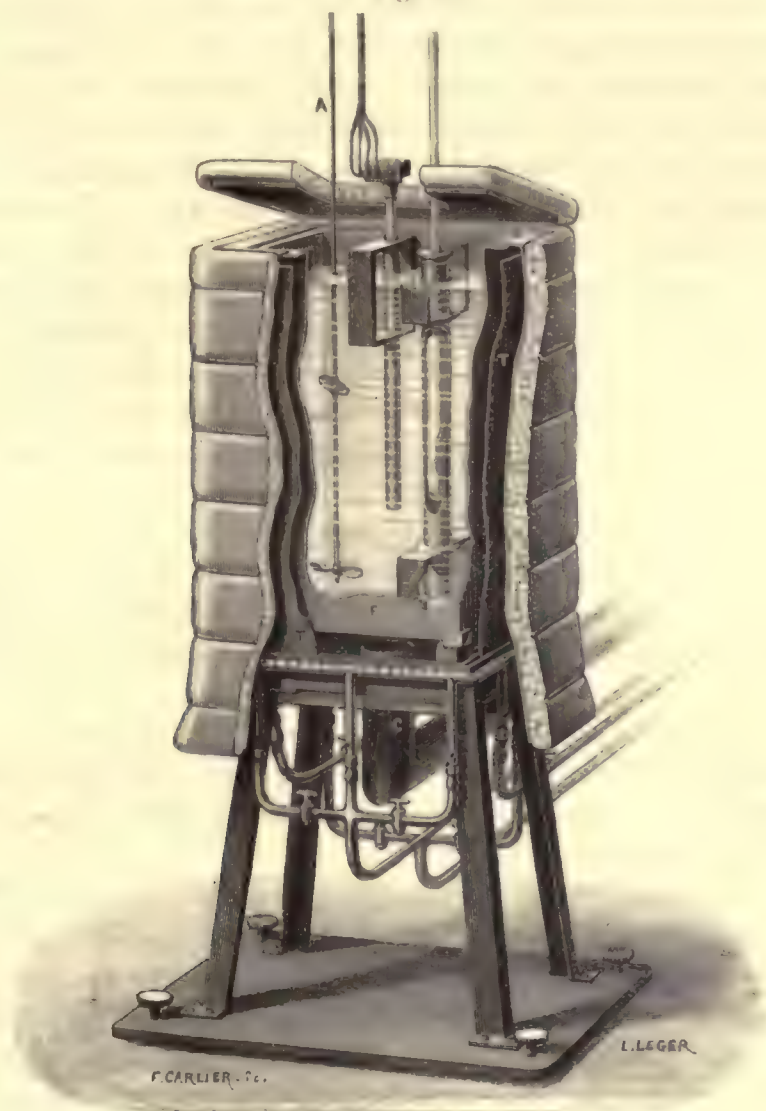
which is the mean of the last group of determinations given on p. 84.

XXXVIII. COMPARISONS AT TEMPERATURES BETWEEN 250° AND 460°.

For the comparisons at high temperatures we constructed a special heating bath, which has proved satisfactory up to the temperatures indicated, and has subsequently been employed up to about 600°.

This apparatus is represented in fig. 19. It consists essentially of a bath of a

Fig. 19.



Bath for High Temperature Comparisons.

F, cast-iron tank holding the mixed nitrates; A, stirrer shaft; C, chimney; T, wall of air-bath cut away to show interior.

mixture of nitrates of potassium and sodium, heated externally by a double circulation of hot gases, and stirred continuously by a system of rotating screws.

The cast-iron vessel which forms the bath has a depth of 50 centims. and an exterior quadrangular section of 20 centims. by 12 centims. ; the angles are slightly rounded at the corners and on the bottom. The interior cross-section of the bath approaches an ellipse, a form found by one of us especially favourable to thorough stirring, when the shaft carrying the rotating screw-blades is placed at one of the foci.

The casting is supported by four substantial feet, 6 centims. in length, on a massive iron plate. This plate is pierced in the centre by a large circular hole, 8 centims. diameter, connected to a suitable sheet-iron chimney, to take away the products of combustion. Around the bath is fixed the first envelope of stout sheet-iron resting on the base-plate, whose height is a little less than that of the bath. Over this is placed a second envelope, open below, slightly pyramidal, and protected on the exterior by several layers of asbestos-card and wool. This rests on the upper edge of the bath, and may easily be detached from the rest of the apparatus.

A special rectangular burner, fitted with several gas taps, is placed round the inner envelope, near the lower opening. The hot gases rise first in the space between the two covers, then descend between the bath and the inner one, finally escaping by the chimney. The top of the bath and the whole of the hot portions of the apparatus which are exposed are prevented, as far as possible, from disturbing the temperature of the room by covering them with thick layers of asbestos-wool.

It would be dangerous to expose the thermometric reservoirs to the direct action of the melted salts. We therefore fixed in the bath thin weldless steel tubes closed at their lower ends, and projecting a few centimetres above the surface of the liquid. The thermometers were introduced into these tubes, which they fitted almost exactly. The tube containing the reservoir of the nitrogen thermometer was provided with a brass lid closely surrounding the capillary tube, a few washers of asbestos completing the joint.

The bath is stirred by two sets of screw-blades fixed to a vertical steel shaft, which extends to a height of about 40 centims. above the top. The upper end of this shaft is suspended directly by a piece of rubber tube from the axis of a small electric motor worked by four accumulators.

The system of heating which we have just described allows a very satisfactory constancy of temperature to be attained, but several hours are required in order to obtain another equilibrium at a different temperature. To facilitate this, the bath was heated continuously during the whole course of the experiments at high temperatures. For the first set of comparisons, which were interrupted by an accident, and which consisted of a small number of measurements, we employed the reservoir of "verre dur" described previously.

In the second, and more complete series, the porcelain reservoir was used throughout.

First Comparisons. (Platinum thermometers, K.8 and K.9, with "verre dur" gas thermometer.)—The comparisons numbered 70 to 72 in the table for K.8, and 25 to 32 in that for K.9 were made during the summer of 1898 with the thermometric reservoir of "verre dur." The following table shows the sequence of the various operations.

Date.	Initial pressure in millims.	Determination of the coefficient of expansion of the nitrogen.	Remarks.
June 9	Reservoir heated to 440° for four hours
" 9	532·877		
" 10	532·879		
" 10	532·869		
" 11	...	0·00366 867	
" 11	...	846	
" 11	...	849	
" 12	532·905		
" 12	532·868	844	
" 13	...	827	
" 17	Reservoir heated to 500°
" 17	Commenced comparisons with thermometer K.9		
" 19	534·320		
" 19	534·298		
" 19	534·307		
" 20	534·295		
" 20	Commenced comparisons with thermometer K.8		

The *comparisons* all being subsequent to the heating of the reservoir to 500°, the nitrogen temperatures have been calculated, assuming for the initial pressure the mean of the observations made *after* the comparisons, viz. :—

$$H = 534·305 \text{ millims.}$$

It will be noticed that this value differs by 1·42 millims.* from the initial pressure observed before the comparisons given previously; this increase is obviously due to the contraction of the reservoir by the annealing effect of the high temperatures. As the reservoir had been heated to about 500° before the observations, we concluded that the contraction was produced entirely before the first measurements.

XXXIX. DETERMINATION OF THE CONSTANTS OF THE NEW GAS THERMOMETER WITH PORCELAIN RESERVOIR.

We have already described the porcelain reservoir and the way it is connected to the manometer tube. It remains to indicate the method by which we have measured

* This variation of pressure corresponds to 0·7 C.

its capacity and pressure coefficient and the necessary new determinations of the "dead space."

(a) *Capacity of the Porcelain Reservoir.*

This was determined by weighing the reservoir empty, and filled with water at 0°. The following are the results of the weighings made:—

Date.	Reservoir empty.	Reservoir filled.	Weight of water.
	grams.	grams.	grams.
August 9	261·974 74		
" 10		427·336 59	165·368 54
" 11	261·961 35		
" 11		427·328 86	165·367 84
" 11	261·960 69		
" 12		427·337 35	165·376 84
" 12	261·960 33		
			Mean = 165·371 07

The volume occupied by this mass of water at 0° C. is

$$V_0 = 165·393 \text{ cub. centims.}$$

This value has been taken as the total capacity up to the extremity of the capillary tube, part of which is included in the "dead space."

(b) *Dilatation of the Porcelain.*

The porcelain reservoir, carefully dried, was connected to the mercury pump, very thoroughly exhausted, and then filled with mercury *in vacuo*. To the end of the capillary was cemented a glass tube about 1 millim. internal diameter, divided into millimetres, whose calibration corrections and internal volume had been previously determined. The whole being placed in melting ice, the level of the mercury was adjusted to a point on this tube, which was carefully noted. Bringing the whole afterwards to 100°, the amount of mercury which escaped was determined by weighing, the necessary corrections being applied to reduce the reading of the meniscus to its original position.

Four determinations were made by this process of the apparent dilatation of mercury in porcelain between 0° and 100°, and a few series of observations were taken at intermediate temperatures. These measurements, about which it is not necessary to enter into further detail, gave after all reductions the following results:—

Temperature.	Dilatation of the reservoir in microlitres, i.e., excess over volume at 0° C.
25.229	33.87
29.995	40.17
39.746	53.74
49.990	66.85
99.792	147.64
99.796	147.28
99.890	148.03
99.905	148.00

[For the dilatation of mercury, which enters into the calculations, the formula found by one of us ('Procès-verbaux des Séances du Comité International,' 1891, p. 37)

$$V_t = V_0[1 + (182008t - 11.3804t^2 + 0.16921t^3) 10^{-9}]$$

was adopted.]

Treated by the method of least squares, these observations give for the cubic dilatation of porcelain the following formula:—

$$V_t = V_0[1 + 0.00000759306t + 0.00000013750t^2].$$

The observations between 0° and 100° which determine the value of the term in t^2 not being numerous, we can consider only the mean dilatation between the extreme points 0° and 100° as having been determined with sufficient accuracy. As, however, it was of importance to know the second term more exactly, as its influence increases at high temperatures, we made a second determination of the dilatation by means of the Fizeau apparatus. The specimen which served for this determination was prepared from a fragment of the capillary tube of a precisely similar reservoir made at the same time at the Imperial Porcelain Factory at Berlin.

The results of this determination, which comprised 37 observations between the temperatures 2° and 82°, are for the linear expansion

$$\alpha_1 = 0.00000268762,$$

$$\beta_1 = 0.000000029873;$$

and for the cubical expansion

$$\alpha_2 = 0.0000080628,$$

$$\beta_2 = 0.00000008983.$$

The two methods give practically the same result for the mean dilatation between 0° and 100°; by the weight thermometer we have

$$\alpha_1 + 100\beta_1 = 0.00000896871,$$

and by the Fizeau method we have

$$\alpha_2 + 100\beta_2 = 0.000\,008\,961\,2.$$

Admitting the coefficient β_2 , deduced from the observations by the Fizeau method, we have calculated the coefficient α_2 from the relation

$$\alpha_2 + 100\beta_2 = 0.000\,008\,968\,71,$$

which gives

$$\alpha_2 = 0.000\,008\,070\,35.$$

We have thus adopted as our final formula for the cubic expansion of Berlin porcelain

$$V_t = V_0(1 + 0.000\,008\,070\,35t + 0.000\,000\,008\,983t).$$

(c) *Pressure Coefficient of the Porcelain Reservoir.*

The measurement of the pressure coefficient of the porcelain reservoir was made in precisely the same way as that of the glass reservoir previously described on p. 75. We determined by three series of observations the variation of volume Δv corresponding to a variation of pressure of 1 millim., obtaining the following results:—

	microlitres.
(1)	$\Delta v = 0.003\,803\,5$
(2)	$\Delta v = 0.003\,701\,7$
(3)	$\Delta v = 0.003\,746\,6$

We have adopted the mean of these three determinations, viz.:—

$$\Delta v = 0.003\,750 \text{ microlitre per millim.}$$

(d) *Determination of the "Dead Space."*

For this determination we followed exactly the method already described on p. 75. The nine weighings made gave divergences from the mean of four parts per thousand. After all reductions we found for the whole volume of the "dead space"

$$v = 709.5 \text{ microlitres.}$$

The effective capacity of the thermometric reservoir being

$$V_0 = 164.805 \text{ cub. centims.,}$$

we have

$$v/V_0 = 0.004\,305.$$

This result, which is appreciably higher than the corresponding one for the

reservoir of "verre dur," was employed for the reduction of all the measurements made with the gas thermometer with porcelain reservoir.

XL. FIRST DETERMINATIONS WITH PORCELAIN GAS THERMOMETER.

The mounting of the gas thermometer being completed, we proceeded to fill the reservoir with nitrogen. The gas was prepared by the process previously described and was thoroughly dried over phosphorus pentoxide. The reservoir was several times pumped out and partially filled with the dry gas, it being heated meanwhile to a temperature of about 250° , and the final filling and adjustment of the pressure was made at the same high temperature.

We give in the following table the measurements of the initial pressure and coefficient of expansion of the nitrogen, made immediately afterwards.

Date.	Initial pressure. H_0 .	Coefficient. α .
	millims.	
September 18	524.591	
" 18	.619	
" 19	.576	
" 19	...	0.003 670 8
" 20	...	669 9
" 20	.592	
" 20	.589	
" 21	.577	
" 21	...	0.003 670 1
" 21	...	3 669 4
" 21	.627	
" 21	.624	
" 22	.584	
" 22	...	0.003 669 4
" 22	...	669 2
" 23	.563	
" 23	.572	
	Mean =	0.003 669 8

The value here found for the coefficient of expansion of nitrogen is slightly higher than that previously obtained with the glass reservoir thermometer (0.003 668 5 instead of 0.003 668 5).

Before proceeding to the experiments at high temperatures, we thought it advisable to heat the porcelain reservoir to the temperature of ebullition of sulphur, to see if under the actual circumstances prolonged exposure to a high temperature would produce a modification of the initial pressure. As is well known, certain bodies retain traces of water or condensed gases up to very high temperatures, and, as the reservoir had been washed with distilled water, there was some ground for appre-

hension that, in spite of the care taken with the filling, it might possibly have retained traces of water.

After a heating of 26 hours above 400° we found in fact an initial pressure considerably greater than that given above, viz. :—

	millims.
October 4	525·359
„ 4	525·361
„ 5	525·341
„ 7	525·348
Mean	<hr/> 525·352

Determinations of the coefficient of expansion gave also a value appreciably greater than the one found previously.

From the mean of four experiments we found

$$\alpha = 0\cdot003\ 674\ 0.$$

Our fears having been justified, the thermometer reservoir was again put into communication with the pump and exhausted, being meanwhile heated to a temperature of about 500° . After several successive exhaustions and partial fillings of gas the reservoir was then pumped out very thoroughly, and after remaining vacuous for 24 hours was filled to the proper pressure with very well dried gas. It was maintained all the time at a temperature approaching 500° .

The following measurements of the initial pressure and coefficient of expansion were then made :—

Date.	Initial pressure.	Coefficient.
October 15	...	0.00366 855
" 16	...	845
" 16	528.853	
" 16	.824	
" 17	.833	
" 17	...	0.00366 830
" 17	...	934
" 18	528.828	
" 18	.806	
" 19	...	0.00366 764
" 19	...	776
" 20	...	769
" 20	...	873
" 21	528.801	
" 22	.848	
" 22	.844	
From October 25 to 29, comparisons with thermometer K.9.		
October 31	528.773	
November 1	.781	
" 1	.773	
" 2	.789	
" 2	...	0.00366 783
" 2	...	742
" 3	.790	
" 5	.734	
" 7	528.746	
" 10	.742	
" 11	.746	
" 11	.739	
From November 12 to 17, comparisons with thermometer K.8.		
November 18	528.759	
" 18	.755	
" 30	...	0.00366 848
" 30	...	764
December 1	...	757
" 1	528.765	
" 1	.735	

From this table it may be seen that the initial pressure diminished during the series of comparisons with K.9 by about 0.05 millim. We have assumed for the reduction of the observations that this diminution was proportional to the time. During the comparisons with thermometer K.8 no sensible diminution of initial pressure was observed.

Comparisons of the Platinum Thermometers with Porcelain Gas Thermometer.

We give in the following table the values of the initial pressure assumed on each

day for the experiments with thermometer K.9. For the coefficient of expansion we have taken the mean of the determinations given above, viz. :—

$$\alpha = 0.003\,668\,11.$$

Date of comparison.	Initial pressure in millims.
October 25	528.807
„ 26	528.802
„ 27	528.797
„ 28	528.792
„ 29	528.787

The comparisons are numbered 33 to 53 in the table for K.9 at the end.

For the calculation of all the comparisons with thermometer K.8 we have taken as the initial pressure the value 528.747 millims. These comparisons are numbered 73 to 91 in the table for K.8 at the end.

Comparisons of Thermometer K.2.

We noticed that during the experiments with K.8 and K.9 above the sulphur point the glass tubes of the platinum thermometers were seriously attacked and showed signs of softening. Some time previously porcelain tubes had been ordered to replace the glass ones, but owing to the delivery of these being inordinately delayed, we were obliged to relinquish the comparisons we had intended to make with K.8 and K.9 at higher temperatures and take in their place a low resistance platinum thermometer, K.2, already provided with a porcelain tube. The initial pressure in the gas thermometer was reduced to 391.88 millims. and a series of 12 comparisons made, the results of which are shown in the table at the end.*

The constants of the gas thermometer were determined in the usual manner before the comparisons. The value found for the coefficient α was 0.003 667 71. We were prevented by an accident from redetermining this coefficient of dilatation *after* the measurements. This is to be regretted, as the preceding determinations showed a systematic diminution in its value which we are unable to explain.

If the coefficient corresponding to an initial pressure of 392 millims. be deduced

* As a confirmation of the general accuracy of the methods of standardization, &c., adopted in our platinum thermometry, we may mention that on the return of the apparatus from France the constants of thermometer K.2 were redetermined at Kew by Dr. CHREE and Mr. HUGO, using the improved Cambridge resistance box, which had just been re-calibrated by them. For the platinum temperature of the sulphur point at 760 millims. pressure they found a value differing only 0.01 from that got at Sèvres, although nearly the whole of the apparatus employed, including the resistance box, leads, and barometer, were of patterns differing materially from those used in France.

from the law previously found by one of us that the departure of the coefficient from that of a perfect gas varies proportionally to the initial pressure, we have

$$\alpha = 0.003\ 666\ 3.$$

This coefficient would give for temperatures near the sulphur point values about $0^{\circ}.2$ higher than those deduced by employing the one directly observed.

We have nevertheless adhered to the latter for the calculation of the temperatures of this series of comparisons, in order to avoid the introduction of any hypothesis.

XLI. EXPLANATION OF THE TABLES OF RESULTS.

The results of the whole of the comparisons made are given in the tables for each thermometer at the end. In these the experiments are arranged in order of ascending temperature. The first three columns give for each experiment the progressive number, the number in our note-books and the date. Columns IV. and V. give pt and d , the value for d being that deduced from the Callendar formula given on p. 39, assuming the value for δ as determined for each thermometer at the sulphur point, and taking our new value for the boiling-point of sulphur at 760 millims. pressure, namely $445^{\circ}.27$, given later on p. 101. Column VI. gives the equivalent on the nitrogen scale of the observed pt , as thus calculated, and Column VII. the temperature on the nitrogen scale as given by the gas thermometer. Column VIII. shows the difference between the calculated and observed values, and Column IX. the constancy of the temperature in each experiment as given by the indication of the platinum thermometer.

XLII. DETERMINATION OF THE BOILING-POINT OF SULPHUR.

After ascertaining that it was possible, by means of the bath of fused nitrates, to make accurate comparisons between the platinum and gas thermometers at temperatures up to about 600° , we saw that by making alternately a determination of the resistance of a platinum thermometer at the boiling-point of sulphur, and a comparison with the gas thermometer near the same temperature, we had a means of obtaining a new determination of the boiling-point on the nitrogen scale. We accordingly made, in an apparatus of the form described by CALLENDAR and GRIFFITHS as the "Meyer tube," a number of determinations of the platinum temperature of sulphur-vapour boiling freely under atmospheric pressure. Readings of the barometer were taken simultaneously with those of the platinum thermometer. The reservoir of the platinum thermometer was protected from contact with any condensed sulphur which might flow down to it from the cooler part of the thermometer above, by surrounding it with an asbestos cone perforated with several holes

in the base and sides to permit free circulation of the sulphur vapour within it.* It is essential for the attainment of a constant temperature that the cone should be sufficiently long to completely cover the resistance-spiral and a certain length of the stem immediately above it.

During the earlier experiments we had considerable difficulty with the sulphur tubes owing to their liability to crack on re-heating, after having once been used. We thus found it convenient, when making several consecutive sulphur point determinations, to keep the sulphur just liquid between the different sets of observations, by means of a small by-pass flame. The establishment of a constant temperature in the sulphur apparatus takes a considerable time; from half-an-hour to an hour was generally allowed after insertion of the thermometer.†

The sulphur we used was obtained from Messrs. BAIRD and TATLOCK, and was made by CHANCE'S process. Though we made no chemical tests of its purity, we have reason to believe that the impurities present, if any, exert practically no influence on the boiling-point, as a large number of determinations made at Kew showed no systematic difference in the behaviour of several different samples. Additional evidence of the purity of the sulphur used is afforded by the remarkable steadiness of the temperature of the vapour, when once the equilibrium is established.

Three independent values for the boiling-point of sulphur were obtained under different circumstances. To the first of these, obtained from the preliminary comparisons of thermometer K.9 with the gas thermometer with reservoir of "verre dur," we attach less weight than to the two subsequent ones, where K.8 and K.9 were compared with the gas thermometer fitted with the porcelain reservoir more suited for high temperatures.

We discuss the observations of the later series, taken with K.8, as an example of the method of reduction followed.

The determinations made with this thermometer of the platinum temperature of the boiling-point of sulphur were eight in number, the corresponding pressures varying from 755 to 762 millims. It is obvious that, from the experiments themselves, the platinum temperature corresponding to 760 millims. could be deduced by the method of least squares, but a formula for the variation of the boiling-point with pressure deduced from so few experiments would, however, be liable to error. We, therefore,

* This form of protector is due to HEYCOCK and NEVILLE, and is described in their paper in 'Trans. Chem. Soc.,' 1895, p. 197.

† In the use of this apparatus there are several precautions to be observed essential for good results. The liquid sulphur in the Meyer tube must extend to some few centimetres above the base plate of the apparatus. The gas burner should preferably be a large solid-flame bunsen, and the flame should be screened from draughts by asbestos-card or by a number of firebricks surrounding the apparatus. The cones are attached to the thermometer by fine iron wire. The asbestos becomes very hard on cooling, but, if, after use, the adhering sulphur is burnt off, the cones can be rendered sufficiently pliable to serve for several determinations.

attempted to collect further evidence on the subject, before proceeding to the final reduction of our results.

CALLENDAR and GRIFFITHS in re-determining the boiling-point of sulphur made no attempt to deduce any formula for the variation of this point with pressure, and, in their subsequent work, apply the one deduced by REGNAULT from his observations made in 1862.

As the results of this investigation of REGNAULT have been differently interpreted by several observers, it may be worth while here to state exactly what experiments REGNAULT made on the subject. The primary object of his work was to determine the influence of large variations of pressure on the boiling-points of a number of substances, rather than to deduce formulæ representing accurately over a limited range the variation for each substance. He made altogether eight experiments with sulphur at pressures between 250 and 3000 millims., the four nearest to the standard pressure of 760 millims. being as follows:—

Temperature on air scale.	Pressure in millims.
418·70	467·45
440·30	679·97
447·71	763·04
485·61	1308·54

In the carrying out of these experiments REGNAULT says he had considerable difficulty, due to violent boiling and also to superheating of the vapour, especially at high pressures.

From the eight experiments REGNAULT calculated a formula for the change of temperature with pressure over the whole range; from this GRIFFITHS finds the value of dt/dp at 760 millims. to be 0·082.

It happens, however, that the experiment made at 763 millims. is one, the result of which diverges more from the calculated value than almost any other, and therefore the value to be taken as the boiling-point at 760 millims. is appreciably uncertain.

The most probable value for this point, as deduced from these observations of REGNAULT, is given by different authorities as $448^{\circ}38$, $448^{\circ}34$, and $447^{\circ}48$.

In view of this uncertainty, and also of the fact that the Meyer tube apparatus is so entirely different in its construction from that employed by REGNAULT, we deemed it advisable to obtain some further evidence as to the validity of the application of REGNAULT'S value of dt/dp to our experiments. As our own observations happened to be all made within a small pressure range, we selected from the records of the platinum thermometers in regular use at Kew Observatory, the results of the different determinations of the sulphur-point made with thermometers K.1 and K.3, and from these, calculated by least squares for each thermometer a formula representing the

variation of pt with pressure, from which, by combination with the known value of $d.pt/dt$, we obtained two concordant values for dt/dp at 760 millims. The mean of these values coincided sufficiently nearly with that of REGNAULT to justify us in adopting the latter for present purposes, and the reduction of our observations to normal pressure is therefore based on the assumption of his value.*

We found that for the thermometers K.8 and K.9 the value of $d.pt/dt$, at the sulphur point, was practically identical with the mean of those previously obtained for the older thermometers, and by assuming this number and combining it with the value calculated from REGNAULT'S experiments for dt/dp , we obtained $d.pt/dp$ for K.8 and K.9.

From this the value of pt_s , the platinum temperature of the sulphur vapour at 760 millims., was then calculated for each experiment, and the mean value for each series taken.

The platinum temperatures found in these comparisons made with each thermometer near the point 445° , and their corresponding values on the nitrogen scale, were then treated by least squares, to obtain from them the nitrogen temperature equivalent to the value of pt_s found previously. Various formulæ for this calculation were tried, the most suitable one being found to be

$$T_s = x + y (pt - pt_s) + z (pt - pt_s)^2$$

where T_s is the nitrogen temperature sought corresponding to pt_s , and x , y and z are constants.†

In this calculation for thermometer K.8 were included the seven experiments numbered 85 to 91 in the table, and in the calculation weights were assigned to the individual experiments according to the constancy of the temperature. On substituting in the original equations of condition the greatest residual was found to be $0^\circ.034$, showing a satisfactory concordance between the values for T_s given by the different comparisons.

* Although we do not wish to give the formula we calculated from the observations made at Kew as the outcome of a new *determination* of dt/dp for sulphur, yet it may be worth while to give an idea of the kind of agreement between the value found and that of REGNAULT, which we adopted for the reduction of our observations. The experiments with thermometer K.1 were made between the extremes of pressure 747 and 773 millims., but the majority of them were only very slightly removed from 760 millims. The series with K.3 was better adapted for the purpose of deducing a formula, the observations being distributed fairly evenly over the range 747 to 769 millims. These two sets of experiments were made by Mr. HUGO, Senior Assistant at Kew Observatory.

If T_s be the boiling-point under 760 millims. pressure, we have for the value at 755 millims. from the formulæ deduced from REGNAULT, and from thermometers K.1 and K.3, the values $(T_s - .41)^\circ$, $(T_s - .43)^\circ$, and $(T_s - .42)^\circ$, respectively.

† For another method of arriving at the value of pt_s and the corresponding T_s leading to a mean result slightly different from that here given, see Appendix II., added while the paper was in press.

From the different series of experiments from which a value can be deduced by this method we have

1st Series	K.9	and glass reservoir	$T_s = 445\cdot27$
2nd	„	K.9 „ porcelain „	$T_s = 445\cdot26$
3rd	„	K.8 „ „ „	$T_s = 445\cdot29$
<hr/>			
Mean	.	.	$= 445\cdot27$

Although we think that the extremely close agreement of these values is to some extent fortuitous, and may give an exaggerated idea of the accuracy attained in our experiments, we think that until more is known concerning the expansion at high temperatures of the material used as thermometric reservoir, $445^{\circ}\cdot27$ may be taken as a close approximation to the temperature attained by the vapour of pure sulphur boiling freely under a pressure of 760 millims. *in the apparatus above described*. Whether this represents the *true* temperature, or whether the indications of the thermometer are affected to any appreciable extent by radiation and other disturbing influences, we have not attempted to consider in detail. We contented ourselves with ascertaining that the form of apparatus we used is capable of giving consistent results, and that the temperature attained in it by the vapour after the steady state has been reached really alters with the barometric pressure. We noticed that the barometer we used, and those platinum thermometers which were provided with *glass* envelopes, appeared to follow changes at very nearly the same rate. Considering that the observations of the boiling-point were only made when the barometer appeared to be fairly steady, we think that any error in the measurement of the corresponding temperatures and pressures due to difference of lag of the two instruments must have been very small.

XLIII. REDUCTION OF RESULTS TO NORMAL SCALE.

In view of the lack of data as to the difference between the various gas scales at high temperatures, we are unable to reduce the results of our comparisons, and the value found for the boiling-point of sulphur, to what they would have been on the scale of the hydrogen thermometer.*

* [Footnote added December 1, 1899.—From the study of the different gas scales previously made by one of us, it appears that between 0° and 100° the point of maximum difference between the hydrogen and nitrogen scales is at 40° , where the nitrogen thermometer reads higher by $0\cdot01$. At 100° the difference between the two scales becomes zero by definition, and above that temperature it changes sign and has a value which appears not to exceed $0\cdot1$ below 600° .

The scale of the constant volume nitrogen thermometer appears not to be independent of the initial pressure; if we may judge by the variation of the coefficient $\frac{1}{p_0} \frac{dp}{dt}$, which approaches that of hydrogen as the pressure diminishes, we may assume that the difference between the scales of the nitrogen and

Nor is it easy to apply to the results on the nitrogen scale the correction necessary to bring them to what should have been found had we been able to employ an initial pressure of 1 metre instead of 528 millims.

As has been pointed out, all our gas temperatures are referred to the *constant-volume* scale. The connection between this and the constant-pressure scale, and the corrections to be applied to each to reduce them to the absolute gas scale, have been calculated by Lord KELVIN and Dr. JOULE from their experiments on the flow of gases through porous plugs. Various formulæ giving this correction have, however, been proposed by KELVIN and JOULE themselves, and by others. In a recent paper by ROSE-INNES* a type of formula is deduced from the same observations, which applies to the results found with all the three gases experimented upon by KELVIN and JOULE. ROSE-INNES† says, "To the degree of approximation to which we are working, therefore, there is no thermodynamic correction needed for a constant-volume gas thermometer. There may be a correction involving *squares* of small quantities, which would appear on a nearer approximation. Such a correction, however, would not be worth taking into account in the case of a thermometer constructed with air or hydrogen, as the unavoidable errors of experiment would certainly be much larger than the correction."

Our result for the boiling-point of sulphur is about $0^{\circ}7$ higher than that of CALLENDAR and GRIFFITHS, but it may be well to point out here that the two values are not necessarily inconsistent. The value of CALLENDAR and GRIFFITHS is given as $444^{\circ}53$ for the boiling-point of sulphur *on the constant-pressure air scale*, the air being taken under an initial pressure of 76 centims.

Our value $445^{\circ}27$ we give as the equivalent of the same temperature *on the scale of the constant-volume nitrogen thermometer*, the nitrogen being taken under the initial pressure of 528 millims. It is impossible, we think, at present to say from

hydrogen thermometers varies directly as the initial pressure. Consequently, in the comparisons between 100° and 200° , where the initial pressure was about 800 millims., the difference between the two scales would be diminished to about four-fifths, and in the comparisons between 200° and 455° to about half of what it would have been with an initial pressure of one metre.

We may also remark that the coefficient of dilatation of air under constant pressure

$$\alpha = 0.003\,674\,9,$$

determined by CALLENDAR and GRIFFITHS and employed by them to calculate the temperatures in their observations, is sensibly higher than that which results from the experiments of REGNAULT,

$$\alpha = 0.003\,670\,0,$$

or the value obtained some time ago by one of us,

$$\alpha = 0.003\,670\,8.$$

The adoption of these latter values would raise the result of CALLENDAR and GRIFFITHS about half a degree.]

* 'Phil. Mag.,' March, 1898.

† *Loc. cit.*, p. 293.

theory what difference should be found between the results in the two cases. CALLENDAR and GRIFFITHS point out, however, that the few observations they made, using their instrument as a constant-volume thermometer, gave a result for the sulphur point about half a degree higher than that found on the constant-pressure scale. If confirmed, this would account for more than half of the difference between the two results.

It may be of interest to calculate what differences there would be between temperatures expressed on CALLENDAR'S air scale and the same temperatures on the nitrogen scale based on the adoption of our value for the boiling-point of sulphur, and on the validity of the δ formula. The adoption of the new value for the sulphur boiling-point— $0^{\circ}\cdot74$ higher than that of CALLENDAR and GRIFFITHS—would raise a δ of 1.500 to 1.5423. The differences between the temperatures deduced by admitting the validity of the parabolic formula in each case are shown in the following table:—

$T_{(Call.)}$	-50°	0°	25°	50°	75°	100°	200°	400°	600°	1000°
$T_{(new)} - T_{(Call.)}$. .	$+0\cdot03$	0°	$-0\cdot008$	$-0\cdot011$	$-0\cdot008$	0	$+0\cdot09$	$+0\cdot57$	$+1\cdot5$	$+5\cdot3$

From the results of our comparisons we might calculate a formula giving the magnitude of a small corrective term to be applied to the temperatures as deduced by the parabolic formula to reduce them to the scale of our nitrogen thermometer. This correction, however, is not the same for the different platinum thermometers we used, and an examination of the differences given in Column VIII. of the tables shows that in some places the corrective terms for the two thermometers differ by a quantity of about the same order as the corrections themselves.

Since, as we have previously explained, our own nitrogen scale is somewhat arbitrary, and its relation to the normal scale of the hydrogen thermometer is only known over a small part of the range covered by the experiments, we would suggest that, for the present, temperatures deduced by the platinum thermometer should be reduced by a parabolic formula. The results thus obtained can always be recalculated and expressed on any scale which may subsequently be adopted as the standard scale for high temperatures.

Although we found it impossible to use hydrogen at high temperatures in our gas thermometer with glass reservoir owing to some chemical action taking place between it and the glass, yet it is quite possible that a suitable material may be found for the construction of a thermometer reservoir in which this gas may be employed at high temperatures.

Until further investigations have been made as to the relations of the various gas scales at high temperatures, and as to the influence of the initial pressure and the effect of impurities and traces of water vapour in the gases employed, and until exact determinations have been made up to high temperatures of the coefficient of expansion of the material used as thermometric reservoir, we think that for the

purposes of high range thermometry a scale deduced by the parabolic formula from that of the platinum thermometer will suffice. In the present state of our knowledge any attempt to improve on such a thermometric scale would be attended with such uncertainties as would probably render it futile.

XLIV. CONCLUSION.

In conclusion, the authors are desirous of expressing their obligation to Dr. BENOIT, Director of the Bureau International des Poids et Mesures, to Professor CAREY FOSTER, Chairman of the Kew Observatory Sub-Committee on Thermometry, and to Dr. CHREE, Superintendent of the Observatory, for continued advice and help throughout the whole of their work. For the loan of several pieces of apparatus they are indebted to Professor SCHUSTER of Manchester, and to M. BROCA of the Ecole de Médecine, Paris, and for help with the calculations to M. MAUDET and to Mdles. DE BAULLER and JUNOT, Assistants at the Bureau International, and to all these they tender their sincere thanks.

TABLE I.—Summary of Experiments with Thermometer K.8. $\delta = 1.5435$.

NOTE.—In the column headed "Observed value on gas scale," for the experiments 1-20 the gas referred to is *hydrogen*; for all subsequent experiments, *nitrogen* is intended.

I. Reference number.	II. Number in book.	III. Date of experiment.	IV. <i>pt.</i>	V. <i>d.</i>	VI. Calculated value on nitrogen scale.	VII. Observed value of gas scale.	VIII. Difference calculated- observed.	IX. Change of temperature during experiment. 1 centim. = $\cdot 04^\circ$, approximately.
First Series.—Comparisons against mercury thermometers in alcohol bath.								
1	20	1897 Dec. 7	-23.897	+ .448	-23.449	-23.446	- .003	First half fall 5 centims., second half con- stant
2	19	" 14	-19.479	+ .352	-19.127	-19.134	+ .007	Small oscillations
3	18	" 7	-10.851	+ .182	-10.669	-10.672	+ .003	Fall $2\frac{1}{2}$ centims.
Second Series.—Comparisons against mercury thermometers in water bath.								
4	17	1897 Nov. 15	+ 2.133	- .032	2.101	+ 2.096	+ .005	Rise 2 centims.
5	16	" 8	Excluded on account of moisture being discovered in the thermometer
6	8	Sept. 23	5.204	- .075	5.129	+ 5.113	+ .016	Very slow fall, then rise
7	15	Nov. 15	7.488	- .106	7.382	+ 7.364	+ .018	Slow rise 1.5 centim.
8	6	Sept. 6	10.300	- .140	10.160	+ 10.144	+ .016	Slow rise, then fall. Compensation
9	7	" 6	15.050	- .196	14.854	+ 14.843	+ .011	Rise $2\frac{1}{2}$ centims.
10	1	Aug. 24	Excluded on account of being done without reversing the battery current
11	3	Sept. 4	20.941	- .253	20.688	+ 20.676	+ .012	Rise $3\frac{1}{2}$ centims.
12	2	Aug. 28	25.350	- .291	25.059	+ 25.050	+ .009	Slow fall, then rise 4 centims.
13	12	Nov. 9	25.520	- .292	25.228	+ 25.217	+ .011	Very small oscillations
14	13	" 10	30.410	- .326	30.084	+ 30.072	+ .012	Very small oscillations
15	5	Sept. 4	36.210	- .356	35.854	+ 35.855	- .001	Rise 4.5 centims.
16	4	" 4	41.543	- .375	41.168	+ 41.172	- .004	Compensation
17	14	Nov. 11	50.425	- .386	50.038	+ 50.037	+ .001	Very small oscillations
Third Series.—Comparisons against mercury thermometers in oil bath.								
18	10	1897 Oct. 28	59.553	- .373	59.180	+ 59.181	- .001	Rise 2 centims.
19	11	" 28	70.582	- .323	70.259	+ 70.262	- .003	Small oscillations
20	9	" 16	78.397	- .264	78.133	+ 78.141	- .008	Rise 2 centims.

TABLE I. (continued).—Summary of Experiments with Thermometer K.8. $\delta = 1.5435$.

NOTE.—In the column headed "Observed value on gas scale," for the experiments 1-20 the gas referred to is *hydrogen*; for all subsequent experiments, *nitrogen* is intended.

I. Reference number.	II. Number in book.	III. Date of experiment.	IV. <i>pt.</i>	V. <i>d.</i>	VI. Calculated value on nitrogen scale.	VII. Observed value on gas scale.	VIII. Difference calculated— observed.	IX. Change of temperature during experiment. 1 centim. = .04, approximately.
Fourth Series.—Comparisons against nitrogen thermometer in oil bath.								
21	23	1898 Mar. 24	88.934	-.154	88.780	88.776	+ .004	Rise 1.6 centim.
22	22	" 24	89.120	-.152	88.968	88.961	+ .007	Rise 2.1 centims.
23	60	May 21	89.880	Error made in registration of results. Can- not be traced
24	54	" 17	89.881	-.142	89.739	89.746	-.007	Very small fall
25	41	Apr. 1	94.780	-.007	94.703	94.710	-.007	Rise 1.2 centim.
26	21	Mar. 23	99.413	-.009	99.404	99.400	+ .004	Constant
27	24	" 24	99.418	-.009	99.409	99.435	-.026	Very small changes. Compensated
28	42	Apr. 1	99.486	-.009	99.478	99.495	-.017	Constant
29	40	" 1	99.543	-.007	99.536	99.543	-.007	Constant
30	47	May 14	99.641	-.005	99.636	99.624	+ .012	Very small fall. Done with wrong battery resistance
31	48	" 16	99.844	-.002	99.842	99.834	+ .008	Constant
32	50	" 16	99.848	-.002	99.846	99.848	-.002	Fall 1 centim.
33	53	" 17	99.848	-.002	99.846	99.849	-.003	Very small changes
34	49	" 16	104.904	+ .082	104.986	105.000	-.014	Very small rise
35	43	Apr. 1	105.102	+ .086	105.188	105.194	-.006	Very small changes
36	25	Mar. 24	108.225	+ .141	108.366	108.389	-.023	Very small changes
37	28	" 26	109.635	+ .167	109.802	109.783	+ .019	Very small fall
38	46	Apr. 2	110.111	+ .176	110.287	110.273	+ .014	Very constant
39	51	May 16	110.302	+ .180	110.482	110.477	+ .005	Small fall
40	44	Apr. 1	111.870	+ .210	112.080	112.078	+ .002	Slow rise, 1.3 centim.
41	45	" 2	114.699	+ .266	114.965	114.954	+ .011	Very constant
42	52	May 16	114.786	+ .267	115.053	115.039	+ .014	Very constant
43	27	Mar. 25	115.365	+ .281	115.646	115.638	+ .008	Very small oscillations
44	26	" 24	115.427	+ .282	115.709	115.725	-.016	Small fall, then rise. Compensated

TABLE I. (continued).—Summary of Experiments with Thermometer K. 8. $\delta = 1.5435$.

NOTE.—In the column headed "Observed value on gas scale," for the experiments 1-20 the gas referred to is *hydrogen*; for all subsequent experiments, *nitrogen* is intended.

I. Reference number.	II. Number in book.	III. Date of experiment.	IV. t .	V. d .	VI. Calculated value on nitrogen scale.	VII. Observed value on gas scale.	VIII. Difference calculated— observed.	IX. Change of temperature during experiment. 1 centim. = .04°, approximately.
Fourth Series (continued).—Comparisons against nitrogen thermometer in oil bath.								
45	31	1898 Mar. 26	118.957	+ .354	119.311	119.258	+ .053	Rise .8 centim.
46	37	" 30	119.631	+ .370	120.001	119.972	+ .029	Rise 1.8 centim.
47	55	May 20	119.708	+ .371	120.079	120.033	+ .046	Very small oscillations
48	30	Mar. 26	127.540	+ .557	128.097	128.042	+ .055	Very small rise
49	56	May 20	128.968	+ .593	129.560	129.527	+ .034	Constant
50	38	Mar. 30	129.748	+ .612	130.360	130.306	+ .054	Constant
51	29	" 26	137.315	+ .815	138.130	138.042	+ .088	Very slow rise
52	57	May 20	137.670	+ .825	138.496	138.456	+ .040	Very slow rise
53	62	" 21	138.328	+ .843	139.171	139.137	+ .034	Very slow rise
54	39	Mar. 30	138.793	+ .856	139.650	139.603	+ .047	Constant
55	58	May 20	145.465	+ 1.053	146.518	146.480	+ .038	Rise .8 centim.
56	36	Mar. 30	147.706	+ 1.122	148.828	148.779	+ .049	Very small changes.
57	34	" 30	150.296	+ 1.205	151.501	151.446	+ .055	Compensated
58	32	" 28	152.542	+ 1.279	153.821	153.769	+ .052	Very small changes.
59	59	May 20	154.639	+ 1.351	155.990	155.940	+ .050	Fall 1.2 centim.
60	61	" 21	154.692	+ 1.352	156.044	156.020	+ .024	Fall 2.5 centims.
61	63	" 21	158.953	+ 1.499	160.452	160.429	+ .023	Rise 1.5 centim.
62	33	Mar. 29	159.333	+ 1.512	160.845	160.788	+ .057	Fall 1 centim.
63	35	" 30	159.891	+ 1.531	161.422	161.384	+ .038	Very constant
64	64	May 23	168.019	+ 1.833	169.852	169.812	+ .040	Very small changes.
65	69	" 24	173.654	+ 2.054	175.708	175.691	+ .017	Rise 1 centim.
66	67	" 24	180.514	+ 2.341	182.855	182.823	+ .032	Very slow fall
67	65	" 23	180.691	+ 2.346	183.037	182.989	+ .048	Rise 5.3 centims.
68	68	" 24	186.027	+ 2.581	188.608	188.608	+ .000	Small changes.
69	66	" 23	187.970	+ 2.670	190.640	190.624	+ .016	Compensated

TABLE I. (continued).—Summary of Experiments with Thermometer K.8. $\delta = 1.5435$.

NOTE.—In the column headed "Observed value on gas scale," for the experiments 1-20 the gas referred to is *hydrogen*; for all subsequent experiments, *nitrogen* is intended.

I. Reference number.	II. Number in book.	III. Date of experiment.	IV. <i>pt.</i>	V. <i>d.</i>	VI. Calculated value of nitrogen scale.	VII. Observed value on gas scale.	VIII. Difference calculated— observed.	IX. Change of temperature during experiment. 1 centim. = .04°, approximately.
Fifth Series.—Comparisons against glass reservoir gas thermometer in nitrate bath. Gas thermometer bulb in steel tube.								
70	72	1898 June 21	275.77	+ 8.06	283.83	283.88	-.05	Fall 4.7 centims.
71	70	" 20	321.10	+ 11.98	333.08	332.91	+ .17	First half rise 7 centims., second half rise 1 centim.
72	71	" 21	339.69	+ 13.84	353.53	353.36	+ .17	Rise 3.6 centims., then slow fall
Sixth Series.—Comparisons against porcelain reservoir gas thermometer in nitrate bath. Both thermometers in steel tubes.								
73	77	1898 Nov. 14	236.839	5.31	242.14	242.10	+ .04	Fall 6 centims.
74	78	" 14	239.561	5.49	245.05	245.02	+ .03	Slow fall, then rapid rise 6.7 centims.
75	80	" 14	291.883	9.35	301.24	301.22	+ .02	Very constant
76	79	" 14	291.907	9.36	301.26	301.23	+ .03	Rise 3.4 centims.
77	74	" 12	312.259	11.16	323.42	323.28	+ .14	Fall 1.2 centim.
78	73	" 12	312.336	11.16	323.50	323.36	+ .14	Very small oscillations
79	76	" 12	333.718	13.22	346.93	346.78	+ .15	Steady, second half rise 2.5 centims.
80	75	" 12	334.300	13.28	347.58	347.43	+ .15	Fall 2.2 centims.
81	82	" 15	347.937	14.70	362.64	362.53	+ .11	Slow fall, then rise 1.2 centim.
82	81	" 15	348.706	14.79	363.49	363.39	+ .10	Slow fall, then slow rise 1.5 centim.
83	84	" 15	392.778	19.93	412.71	412.65	+ .06	Very slow rise .4 centim.
84	83	" 15	393.858	20.07	413.92	414.04	-.08	Small oscillations
85	85	" 16	414.472	22.75	437.23	437.15	+ .08	Large rise 9 centims.
86	86	" 16	414.851	22.81	437.66	437.61	+ .05	Fall 2.6 centims., then rise 2 centims.
87	88	" 17	419.563	23.46	443.02	443.06	-.04	Rise 3 centims.
88	89	" 17	419.972	23.52	443.49	443.52	-.03	Rise 7.5 centims.
89	90	" 17	422.085	23.81	445.89	445.87	+ .02	Very slow fall, .5 centim.
90	91	" 17	422.107	23.81	445.92	445.89	+ .03	Very constant
91	87	" 16	430.681	25.06	455.74	455.54	+ .20	Rise 3 centims.

TABLE II.—Summary of Comparisons with Platinum Thermometer K.9. $\delta = 1.5472$.

NOTE.—In the column headed "Observed value on gas scale," for experiments 1-6 the gas referred to is *hydrogen*; for all subsequent experiments, *nitrogen* is intended.

I. Reference number.	II. Number in book.	III. Date of experiment.	IV. <i>pt.</i>	V. <i>d.</i>	VI. Calculated value on nitrogen scale.	VII. Observed value on gas scale.	VIII. Difference calculated— observed.	IX. Change of temperature during experiment. 1 centim. = .2, approximately.
First Series.—Comparisons against mercury thermometers.								
1	19	1898 June 3	10.242	-.140	10.102	10.090	+ .012	Small changes. Rise 4.4 centims.
2	20	" 3	20.023	-.245	19.778	19.774	+ .004	Small rise, then steady
3	21	" 4	30.149	-.323	29.826	29.819	+ .007	Compensation
4	22	" 4	40.378	-.371	40.007	40.004	+ .003	Compensation
5	23	" 4	50.278	-.386	49.892	49.901	-.009	Rise 2 centims. in each half
6	24	" 4	60.203	-.370	59.833	59.842	-.009	
Second Series.—Comparisons against glass reservoir gas thermometer in oil bath.								
7	12	1898 June 1	68.493	-.334	68.159	68.171	-.012	Small changes. Rise 2 centims.
8	9	" 1	80.552	-.245	80.307	80.314	-.007	Rise 1.5 centim.
9	10	" 1	90.023	-.140	89.883	89.901	-.018	Very constant
10	6	May 31	99.072	-.014	99.058	99.068	-.010	Very small rise
11	11	June 1	99.158	-.012	99.146	99.179	-.033	Very small fall
12	7	May 31	109.006	+.156	109.162	109.174	-.012	Very small fall
13	8	" 31	116.271	+.300	116.571	116.577	-.006	Fall 1.5 centim.
14	13	June 2	128.458	+.581	129.039	129.050	-.011	Large fall, 8.7 centims.
15	14	" 2	138.790	+.858	139.648	139.667	-.019	Very small rise
16	18	" 2	140.660	+.910	141.570	141.588	-.018	Rise 2 centims.
17	15	" 2	149.374	+.177	150.551	150.591	-.040	Fall 2½ centims.
18	16	" 2	157.548	+.1451	158.999	159.040	-.041	Slight fall
19	17	" 2	172.575	+.2014	174.589	174.565	+.024	Large rise, 8 centims.
20	5	May 31	176.415	+.2169	178.584	178.554	+.030	Very slow fall
21	3	" 30	181.023	+.2365	183.388	183.387	+.001	Nearly compensated
22	4	" 31	181.301	+.2377	183.678	183.640	+.038	Very constant
23	1	" 30	185.179	+.2545	187.724	187.744	-.020	
24	2	" 30						

TABLE II. (continued).—Summary of Comparisons with Platinum Thermometer K.9. $\delta = 1.5472$.NOTE.—In the column headed "Observed value on gas scale," for experiments 1-6 the gas referred to is *hydrogen*; for all subsequent experiments, *nitrogen* is intended.

I. Reference number.	II. Number in book.	III. Date of experiment.	IV. <i>pt.</i>	V. <i>d.</i>	VI. Calculated value on nitrogen scale.	VII. Observed value on gas scale.	VIII. Difference calculated - observed.	IX. Change of temperature during experiment. 1 centim. = .2°, approximately.
Third Series.—Comparisons against glass reservoir gas thermometer in nitrate bath. Gas thermometer bulb <i>only</i> in steel tube.								
25	28	1898 June 18	251.49	+ 6.28	257.77	257.79	-.02	Slow fall
26	29	" 18	297.09	+ 9.82	306.91	306.97	-.06	Compensated
27	30	" 18	346.77	+ 14.61	361.38	361.40	-.02	Fall 4 centims.
28	31	" 18	385.58	+ 19.08	404.64	404.75	-.11	Fall 2½ centims.
29	32	" 18	416.00	+ 23.02	439.02	439.13	-.11	Fall 6 centims.
30	25	" 17	416.61	+ 23.10	439.71	439.86	-.15	Compensated
31	27	" 17	417.32	+ 23.21	440.53	440.45	+.08	Compensated
32	26	" 17	425.31	+ 24.32	449.63	449.53	+.10	Large fall, 9 centims.
Fourth Series.—Comparisons against porcelain reservoir gas thermometer in nitrate bath. <i>Both</i> thermometers in steel tubes.								
33	38	1898 Oct. 26	241.380	+ 5.617	247.00	246.94	+.06	Rise 4.2 centims.
34	39	" 26	246.664	+ 5.953	252.62	252.50	+.12	Rise 7.8 centims.
35	40	" 26	247.516	+ 6.012	253.53	253.43	+.10	Rise 7.8 centims.
36	41	" 26	247.800	+ 6.030	253.83	253.74	+.09	Rise 5.7 centims.
37	42	" 27	280.625	+ 8.458	289.08	288.97	+.11	Very constant
38	43	" 27	284.328	+ 8.751	293.08	292.86	+.22	Rise 2 centims.
39	45	" 27	317.138	+ 11.641	328.78	328.56	+.22	Compensated
40	44	" 27	317.333	+ 11.660	328.99	328.76	+.23	Compensated
41	33	" 25	318.402	+ 11.759	330.16	329.88	+.28	Large rise, 13.7 centims.
42	34	" 25	319.484	+ 11.861	331.34	331.08	+.26	Rise 5.5 centims.
43	35	" 25	319.523	+ 11.864	331.39	331.13	+.26	Very constant
44	46	" 28	349.749	+ 14.933	364.68	364.43	+.25	Very constant
45	47	" 28	349.764	+ 14.936	364.70	364.46	+.24	Slight fall
46	49	" 28	386.868	+ 19.241	406.11	405.92	+.19	Slow rise, 2 centims.
47	48	" 28	386.999	+ 19.256	406.26	406.09	+.17	Fall 6.4 centims.
48	36	" 25	397.090	+ 20.523	417.61	417.28	+.33	Very small rise
49	37	" 25	398.380	+ 20.657	419.04	418.70	+.34	Fast rise, 10 centims.
50	52	" 29	408.348	+ 21.986	430.33	430.25	+.08	Fall 5 centims.
51	53	" 29	408.587	+ 22.020	430.61	430.49	+.12	Rise 4.7 centims.
52	50	" 29	424.922	+ 24.262	449.18	449.12	+.06	Very slight fall
53	51	" 29	426.258	+ 24.447	450.70	450.58	+.12	Constant

TABLE III.—Summary of Observations with Platinum Thermometer K.2. $\delta = 1.554$.

I. Reference number.	II. Number in book.	III. Date.	IV. <i>pt.</i>	V. <i>d.</i>	VI. T calculated on nitrogen scale.	VII. T observed on nitrogen scale.	VIII. Calculated— observed.	IX. Constancy of temperature in the experiment. 1 centim. = .2', approximately.
1	4	1898 Dec. 16	403.11	+21.41	424.52	424.27	+ .25	Steady, then rise of .8 centim.
2	5	" 16	430.62	+25.20	455.82	455.60	+ .22	Fall .5 centim., then steady
3	10	" 16	431.25	+25.29	456.54	456.36	+ .18	Fall in first half 1 centim., in second .7 centim.
4	9	" 13	437.34	+26.18	463.52	463.17	+ .35	Rise 2.3 centim.
5	7	" 13	437.72	+26.24	463.96	463.52	+ .44	Constant
6	8	" 15	447.48	+27.70	475.18	475.04	+ .14	Slow rise
7	11	" 14	489.20	+34.48	523.68	523.42	+ .26	Fall .4 centim., then rise .9 centim.
8	12	" 14	490.55	+34.71	525.26	525.05	+ .21	Fall 1.4 centim.
9	6	" 13	493.77	+35.26	529.03	528.62	+ .41	Fall .2 centim., then rise 1 centim.
10	3	" 13	494.64	+35.42	530.06	529.68	+ .38	Rise 2.3 centims., then fall. Compensated
11	2	" 14	541.92	+44.29	586.21	586.05	+ .16	Fall 1.6 centim.
12	1	" 14	542.23	+44.35	586.58	586.46	+ .12	Rise 2.5 centims., then fall .5 centim.

APPENDIX I.

With a view to facilitating the calculations involved in platinum thermometry, we give, as an appendix, several tables calculated by Mdlle. DE BAULLER and M. MAUDET, of the Bureau International, which have proved of great utility during our work.

Table I. gives from -40° to 460° the values of $\left[\left(\frac{T}{100}\right)^2 - \frac{T}{100}\right]$, and the product of this quantity into a number of different values of δ . It is used for deducing pt from given values of T .

Table II. is for the resolution of the converse problem, and gives T corresponding to different values of pt for thermometers having a δ between 1.54 and 1.57 . At the side are given differences for interpolation between the whole degrees.

Table III. is for the reduction of the steam points, and is extracted from the table calculated by M. BROCH from the results of REGNAULT for the boiling-point of water under different pressures.

Table IV. is for reducing to its equivalent in mercury pressure the excess of pressure of the steam in a boiling-point determination, as measured in millimetres of water.

Table V. is for converting to the platinum scale the temperature of the steam as obtained from Table III.

As an example of the use of some of these tables, we give the following:—

Let the resistance in ice of a certain platinum thermometer whose $\delta = 1.500$ be 2.57827 ohms, and let its resistance in steam be 3.57298 ohms, the barometric height at the time, corrected for temperature and reduced to sea level and latitude 45° , being 749.96 millims., and the excess of the steam pressure over that of the atmosphere being 1.8 millim. of water. Find the resistance corresponding to 100° .

From Table IV. the mercury pressure corresponding to 1.8 millim. of water $= 0.13$ millim. Adding this to the barometric height we obtain 750.09 millims. as the total pressure of the steam. Then from Table III. we obtain, as the temperature of the steam at this pressure, $99^{\circ}.6343$.

For $\delta = 1.500$ we find from Table V. that the platinum temperature corresponding to $99^{\circ}.6343$ is $99^{\circ}.6343 + 0^{\circ}.0055 = 99^{\circ}.6398$.

Therefore the change of resistance between the	Ohms.
platinum temperatures 0° and 99°·6398 is .	$(3·57298 - 2·57827) = 0·99471$
And so F.I. (the fundamental interval, <i>i.e.</i> , the	$\left. \vphantom{\begin{array}{l} \text{change between } 0^\circ \text{ and } 100^\circ \end{array}} \right\} = \frac{0·99471 \times 100}{99·6398} = 0·99831$
change between 0° and 100°)	
Therefore, resistance at 100°	$= 3·57658$

We append also the various formulæ showing the relations of each of the four quantities T , pt , d , and δ to the others, viz:—

$$d \equiv T - pt = \delta \left[\left(\frac{T}{100} \right)^2 - \frac{T}{100} \right] = \left(\frac{5000}{\delta} + 50 \right) - pt - \sqrt{\left(\frac{5000}{\delta} + 50 \right)^2 - \frac{10000pt}{\delta}},$$

$$T = pt + d = \left(\frac{5000}{\delta} + 50 \right) - \sqrt{\left(\frac{5000}{\delta} + 50 \right)^2 - \frac{10000pt}{\delta}},$$

$$pt = T - d = T - \delta \left[\left(\frac{T}{100} \right)^2 - \frac{T}{100} \right].$$

APPENDIX TABLE I.—To find d for given values of T and δ . Deduced from the formula $d = \delta \left[\left(\frac{T}{100} \right)^2 - \frac{T}{100} \right]$.

T.	$\left(\frac{T}{100} \right)^2 - \frac{T}{100}$	$\hat{e} = 1.500$.	$\hat{e} = 1.510$.	$\hat{e} = 1.520$.	$\hat{e} = 1.530$.	$\hat{e} = 1.540$.	$\hat{e} = 1.550$.	$\hat{e} = 1.560$.	$\hat{e} = 1.570$.	$\hat{e} = 1.580$.	$\hat{e} = 1.590$.	$\hat{e} = 1.600$.
-40	+0.5600	+0.8400	+0.8456	+0.8512	+0.8568	+0.8624	+0.8680	+0.8736	+0.8792	+0.8848	+0.8904	+0.8960
-35	+0.4725	+0.7087	+0.7134	+0.7182	+0.7229	+0.7276	+0.7324	+0.7371	+0.7418	+0.7465	+0.7513	+0.7560
-30	+0.3900	+0.5850	+0.5889	+0.5928	+0.5967	+0.6006	+0.6045	+0.6084	+0.6123	+0.6162	+0.6201	+0.6240
-25	+0.3125	+0.4687	+0.4719	+0.4750	+0.4781	+0.4812	+0.4844	+0.4875	+0.4906	+0.4937	+0.4969	+0.5000
-20	+0.2400	+0.3600	+0.3624	+0.3648	+0.3672	+0.3696	+0.3720	+0.3744	+0.3768	+0.3792	+0.3816	+0.3840
-15	+0.1725	+0.2587	+0.2605	+0.2622	+0.2639	+0.2656	+0.2674	+0.2691	+0.2708	+0.2725	+0.2743	+0.2760
-10	+0.1100	+0.1650	+0.1661	+0.1672	+0.1683	+0.1694	+0.1705	+0.1716	+0.1727	+0.1738	+0.1749	+0.1760
-5	+0.0525	+0.0787	+0.0793	+0.0798	+0.0803	+0.0808	+0.0814	+0.0819	+0.0824	+0.0829	+0.0835	+0.0840
0	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000
1	-0.0099	-0.0148	-0.0149	-0.0150	-0.0151	-0.0152	-0.0153	-0.0154	-0.0155	-0.0156	-0.0157	-0.0158
2	-0.0196	-0.0294	-0.0296	-0.0298	-0.0300	-0.0302	-0.0304	-0.0306	-0.0308	-0.0310	-0.0312	-0.0314
3	-0.0291	-0.0436	-0.0439	-0.0442	-0.0445	-0.0448	-0.0451	-0.0454	-0.0457	-0.0460	-0.0463	-0.0466
4	-0.0384	-0.0576	-0.0580	-0.0584	-0.0588	-0.0591	-0.0595	-0.0599	-0.0603	-0.0607	-0.0611	-0.0614
5	-0.0475	-0.0712	-0.0717	-0.0722	-0.0727	-0.0731	-0.0736	-0.0741	-0.0746	-0.0750	-0.0755	-0.0760
6	-0.0564	-0.0846	-0.0852	-0.0857	-0.0863	-0.0869	-0.0874	-0.0880	-0.0885	-0.0891	-0.0897	-0.0902
7	-0.0651	-0.0976	-0.0983	-0.0990	-0.0996	-0.1003	-0.1009	-0.1016	-0.1022	-0.1029	-0.1035	-0.1042
8	-0.0736	-0.1104	-0.1111	-0.1119	-0.1126	-0.1133	-0.1142	-0.1148	-0.1156	-0.1163	-0.1170	-0.1178
9	-0.0819	-0.1228	-0.1237	-0.1245	-0.1253	-0.1261	-0.1269	-0.1278	-0.1286	-0.1294	-0.1302	-0.1310
10	-0.0900	-0.1350	-0.1359	-0.1368	-0.1377	-0.1386	-0.1395	-0.1404	-0.1413	-0.1422	-0.1431	-0.1440
11	-0.0979	-0.1468	-0.1478	-0.1488	-0.1498	-0.1508	-0.1517	-0.1527	-0.1537	-0.1547	-0.1557	-0.1566
12	-0.1056	-0.1584	-0.1595	-0.1605	-0.1616	-0.1626	-0.1637	-0.1647	-0.1658	-0.1668	-0.1679	-0.1690
13	-0.1131	-0.1696	-0.1708	-0.1719	-0.1730	-0.1742	-0.1753	-0.1764	-0.1776	-0.1787	-0.1798	-0.1810
14	-0.1204	-0.1806	-0.1818	-0.1830	-0.1842	-0.1854	-0.1866	-0.1878	-0.1890	-0.1902	-0.1914	-0.1926
15	-0.1275	-0.1912	-0.1925	-0.1938	-0.1951	-0.1963	-0.1976	-0.1989	-0.2002	-0.2014	-0.2027	-0.2040
16	-0.1344	-0.2016	-0.2029	-0.2043	-0.2056	-0.2070	-0.2083	-0.2097	-0.2110	-0.2124	-0.2137	-0.2150
17	-0.1411	-0.2116	-0.2131	-0.2145	-0.2159	-0.2173	-0.2187	-0.2201	-0.2215	-0.2229	-0.2243	-0.2258
18	-0.1476	-0.2214	-0.2229	-0.2244	-0.2258	-0.2273	-0.2288	-0.2303	-0.2317	-0.2332	-0.2347	-0.2362
19	-0.1539	-0.2308	-0.2324	-0.2339	-0.2355	-0.2370	-0.2385	-0.2401	-0.2416	-0.2432	-0.2447	-0.2462
20	-0.1600	-0.2400	-0.2416	-0.2432	-0.2448	-0.2464	-0.2480	-0.2496	-0.2512	-0.2528	-0.2544	-0.2560
21	-0.1659	-0.2488	-0.2505	-0.2522	-0.2538	-0.2555	-0.2571	-0.2588	-0.2605	-0.2621	-0.2638	-0.2654
22	-0.1716	-0.2574	-0.2591	-0.2608	-0.2625	-0.2643	-0.2660	-0.2677	-0.2694	-0.2711	-0.2728	-0.2746
23	-0.1771	-0.2656	-0.2674	-0.2692	-0.2710	-0.2727	-0.2745	-0.2763	-0.2780	-0.2798	-0.2816	-0.2834
24	-0.1824	-0.2736	-0.2754	-0.2772	-0.2791	-0.2809	-0.2827	-0.2845	-0.2864	-0.2882	-0.2900	-0.2918
25	-0.1875	-0.2812	-0.2831	-0.2850	-0.2869	-0.2887	-0.2906	-0.2925	-0.2944	-0.2962	-0.2981	-0.3000
26	-0.1924	-0.2886	-0.2905	-0.2924	-0.2944	-0.2963	-0.2982	-0.3001	-0.3021	-0.3040	-0.3059	-0.3078

APPENDIX TABLE I. (continued).—To find d for given values of T and δ . Deduced from the formula $d = \delta \left[\left(\frac{T}{100} \right)^2 - \frac{T}{100} \right]$.

T.	$\left(\frac{t}{100} \right)^2 - \frac{t}{100}$	$\delta = 1.500.$	$\delta = 1.510.$	$\delta = 1.520.$	$\delta = 1.530.$	$\delta = 1.540.$	$\delta = 1.550.$	$\delta = 1.560.$	$\delta = 1.570.$	$\delta = 1.580.$	$\delta = 1.590.$	$\delta = 1.600.$
27	-0.1971	-0.2956	-0.2976	-0.2996	-0.3016	-0.3035	-0.3055	-0.3075	-0.3094	-0.3114	-0.3134	-0.3154
28	-0.2016	-0.3024	-0.3044	-0.3064	-0.3084	-0.3105	-0.3125	-0.3145	-0.3165	-0.3185	-0.3205	-0.3226
29	-0.2059	-0.3088	-0.3109	-0.3130	-0.3150	-0.3171	-0.3191	-0.3212	-0.3233	-0.3253	-0.3274	-0.3294
30	-0.2100	-0.3150	-0.3171	-0.3192	-0.3213	-0.3234	-0.3255	-0.3276	-0.3297	-0.3318	-0.3339	-0.3360
31	-0.2139	-0.3208	-0.3230	-0.3251	-0.3273	-0.3294	-0.3315	-0.3337	-0.3358	-0.3380	-0.3401	-0.3422
32	-0.2176	-0.3264	-0.3286	-0.3308	-0.3329	-0.3351	-0.3373	-0.3395	-0.3416	-0.3438	-0.3460	-0.3482
33	-0.2211	-0.3316	-0.3338	-0.3361	-0.3383	-0.3405	-0.3427	-0.3449	-0.3471	-0.3493	-0.3515	-0.3538
34	-0.2244	-0.3366	-0.3388	-0.3411	-0.3433	-0.3456	-0.3478	-0.3501	-0.3523	-0.3546	-0.3568	-0.3590
35	-0.2275	-0.3412	-0.3435	-0.3458	-0.3481	-0.3503	-0.3526	-0.3549	-0.3572	-0.3594	-0.3617	-0.3640
36	-0.2304	-0.3456	-0.3479	-0.3502	-0.3525	-0.3548	-0.3571	-0.3594	-0.3617	-0.3640	-0.3663	-0.3686
37	-0.2331	-0.3496	-0.3520	-0.3543	-0.3566	-0.3590	-0.3613	-0.3636	-0.3660	-0.3683	-0.3706	-0.3730
38	-0.2356	-0.3534	-0.3558	-0.3581	-0.3605	-0.3628	-0.3652	-0.3675	-0.3699	-0.3722	-0.3746	-0.3770
39	-0.2379	-0.3568	-0.3592	-0.3616	-0.3640	-0.3664	-0.3687	-0.3711	-0.3735	-0.3759	-0.3783	-0.3806
40	-0.2400	-0.3600	-0.3624	-0.3648	-0.3672	-0.3696	-0.3720	-0.3744	-0.3768	-0.3792	-0.3816	-0.3840
41	-0.2419	-0.3628	-0.3653	-0.3677	-0.3701	-0.3725	-0.3749	-0.3774	-0.3798	-0.3822	-0.3846	-0.3870
42	-0.2436	-0.3654	-0.3678	-0.3703	-0.3727	-0.3751	-0.3776	-0.3800	-0.3825	-0.3849	-0.3873	-0.3898
43	-0.2451	-0.3676	-0.3701	-0.3726	-0.3750	-0.3775	-0.3799	-0.3824	-0.3848	-0.3873	-0.3897	-0.3922
44	-0.2464	-0.3696	-0.3721	-0.3745	-0.3770	-0.3795	-0.3819	-0.3844	-0.3868	-0.3893	-0.3918	-0.3942
45	-0.2475	-0.3712	-0.3737	-0.3762	-0.3787	-0.3811	-0.3836	-0.3861	-0.3886	-0.3910	-0.3935	-0.3960
46	-0.2484	-0.3726	-0.3751	-0.3776	-0.3801	-0.3825	-0.3850	-0.3875	-0.3900	-0.3925	-0.3950	-0.3974
47	-0.2491	-0.3736	-0.3761	-0.3786	-0.3811	-0.3836	-0.3861	-0.3886	-0.3911	-0.3936	-0.3961	-0.3986
48	-0.2496	-0.3744	-0.3769	-0.3794	-0.3819	-0.3844	-0.3869	-0.3894	-0.3919	-0.3944	-0.3969	-0.3994
49	-0.2499	-0.3748	-0.3773	-0.3798	-0.3823	-0.3848	-0.3873	-0.3898	-0.3923	-0.3948	-0.3973	-0.3998
50	-0.2500	-0.3750	-0.3775	-0.3800	-0.3825	-0.3850	-0.3875	-0.3900	-0.3925	-0.3950	-0.3975	-0.4000
+105	+0.0525	+0.0787	+0.0793	+0.0798	+0.0803	+0.0808	+0.0814	+0.0819	+0.0824	+0.0829	+0.0835	+0.0840
+110	+0.1100	+0.1650	+0.1661	+0.1672	+0.1683	+0.1694	+0.1705	+0.1716	+0.1727	+0.1738	+0.1749	+0.1760
+115	+0.1725	+0.2587	+0.2605	+0.2622	+0.2639	+0.2656	+0.2674	+0.2691	+0.2708	+0.2725	+0.2743	+0.2760
+120	+0.2400	+0.3600	+0.3624	+0.3648	+0.3672	+0.3696	+0.3720	+0.3744	+0.3768	+0.3792	+0.3816	+0.3840
+125	+0.3125	+0.4687	+0.4719	+0.4750	+0.4781	+0.4812	+0.4844	+0.4875	+0.4906	+0.4937	+0.4969	+0.5000
+130	+0.3900	+0.5850	+0.5889	+0.5928	+0.5967	+0.6006	+0.6045	+0.6084	+0.6123	+0.6162	+0.6201	+0.6240
+135	+0.4725	+0.7087	+0.7134	+0.7182	+0.7229	+0.7276	+0.7324	+0.7371	+0.7418	+0.7465	+0.7513	+0.7560
+140	+0.5600	+0.8400	+0.8456	+0.8512	+0.8568	+0.8624	+0.8680	+0.8736	+0.8792	+0.8848	+0.8904	+0.8960
+145	+0.6525	+0.9787	+0.9853	+0.9918	+0.9983	+1.0048	+1.0114	+1.0179	+1.0244	+1.0309	+1.0375	+1.0440
+150	+0.7500	+1.1250	+1.1325	+1.1400	+1.1470	+1.1550	+1.1625	+1.1700	+1.1775	+1.1850	+1.1925	+1.2000
+155	+0.8525	+1.2787	+1.2873	+1.2958	+1.3043	+1.3128	+1.3214	+1.3299	+1.3384	+1.3469	+1.3555	+1.3640

APPENDIX TABLE I. (continued).—To find d for given values of T and δ . Deduced from the formula $d = \delta \left[\left(\frac{T}{100} \right)^2 - \frac{T}{100} \right]$.

T.	$\left(\frac{T}{100} \right)^2 - \frac{T}{100}$	$\delta = 1.500.$	$\delta = 1.510.$	$\delta = 1.520.$	$\delta = 1.530.$	$\delta = 1.540.$	$\delta = 1.550.$	$\delta = 1.560.$	$\delta = 1.570.$	$\delta = 1.580.$	$\delta = 1.590.$	$\delta = 1.600.$
+160	+0.9600	+1.4400	+1.4496	+1.4592	+1.4688	+1.4784	+1.4880	+1.4976	+1.5072	+1.5168	+1.5264	+1.5360
+165	+1.0725	+1.6087	+1.6195	+1.6302	+1.6409	+1.6516	+1.6624	+1.6731	+1.6838	+1.6945	+1.7053	+1.7160
+170	+1.1900	+1.7850	+1.7969	+1.8088	+1.8207	+1.8326	+1.8445	+1.8564	+1.8683	+1.8802	+1.8921	+1.9040
+175	+1.3125	+1.9687	+1.9819	+1.9950	+2.0081	+2.0212	+2.0344	+2.0475	+2.0606	+2.0737	+2.0869	+2.1000
+180	+1.4400	+2.1600	+2.1744	+2.1888	+2.2032	+2.2176	+2.2320	+2.2464	+2.2608	+2.2752	+2.2896	+2.3040
+185	+1.5725	+2.3587	+2.3745	+2.3902	+2.4059	+2.4216	+2.4374	+2.4531	+2.4688	+2.4845	+2.5003	+2.5160
+190	+1.7100	+2.5650	+2.5821	+2.5992	+2.6163	+2.6334	+2.6505	+2.6676	+2.6847	+2.7018	+2.7189	+2.7360
+195	+1.8525	+2.7787	+2.7973	+2.8158	+2.8343	+2.8528	+2.8714	+2.8899	+2.9084	+2.9269	+2.9455	+2.9640
+200	+2.0000	+3.0000	+3.0200	+3.0400	+3.0600	+3.0800	+3.1000	+3.1200	+3.1400	+3.1600	+3.1800	+3.2000
+205	+2.1525	+3.2287	+3.2503	+3.2718	+3.2933	+3.3148	+3.3364	+3.3579	+3.3794	+3.4009	+3.4225	+3.4440
+210	+2.3100	+3.4650	+3.4881	+3.5112	+3.5343	+3.5574	+3.5805	+3.6036	+3.6267	+3.6498	+3.6729	+3.6960
+215	+2.4725	+3.7087	+3.7335	+3.7582	+3.7829	+3.8076	+3.8324	+3.8571	+3.8818	+3.9065	+3.9313	+3.9560
+220	+2.6400	+3.9600	+3.9864	+4.0128	+4.0392	+4.0656	+4.0920	+4.1184	+4.1448	+4.1712	+4.1976	+4.2240
+225	+2.8125	+4.2187	+4.2469	+4.2750	+4.3031	+4.3312	+4.3594	+4.3875	+4.4156	+4.4437	+4.4719	+4.5000
+230	+2.9900	+4.4850	+4.5149	+4.5448	+4.5747	+4.6046	+4.6345	+4.6644	+4.6943	+4.7242	+4.7541	+4.7840
+235	+3.1725	+4.7587	+4.7905	+4.8222	+4.8539	+4.8856	+4.9174	+4.9491	+4.9808	+5.0125	+5.0443	+5.0760
+240	+3.3600	+5.0400	+5.0736	+5.1072	+5.1408	+5.1744	+5.2080	+5.2416	+5.2752	+5.3088	+5.3424	+5.3760
+245	+3.5525	+5.3287	+5.3643	+5.3998	+5.4353	+5.4708	+5.5064	+5.5419	+5.5774	+5.6129	+5.6485	+5.6840
+250	+3.7500	+5.6250	+5.6625	+5.7000	+5.7375	+5.7750	+5.8125	+5.8500	+5.8875	+5.9250	+5.9625	+6.0000
+255	+3.9525	+5.9287	+5.9683	+6.0078	+6.0473	+6.0868	+6.1264	+6.1659	+6.2054	+6.2449	+6.2845	+6.3240
+260	+4.1600	+6.2400	+6.2816	+6.3232	+6.3648	+6.4064	+6.4480	+6.4896	+6.5312	+6.5728	+6.6144	+6.6560
+265	+4.3725	+6.5587	+6.6025	+6.6462	+6.6899	+6.7336	+6.7774	+6.8211	+6.8648	+6.9085	+6.9523	+6.9960
+270	+4.5900	+6.8850	+6.9309	+6.9768	+7.0227	+7.0686	+7.1145	+7.1604	+7.2063	+7.2522	+7.2981	+7.3440
+275	+4.8125	+7.2187	+7.2669	+7.3150	+7.3631	+7.4112	+7.4594	+7.5075	+7.5556	+7.6037	+7.6519	+7.7000
+280	+5.0400	+7.5600	+7.6104	+7.6608	+7.7112	+7.7616	+7.8120	+7.8624	+7.9128	+7.9632	+8.0136	+8.0640
+285	+5.2725	+7.9087	+7.9615	+8.0142	+8.0669	+8.1196	+8.1724	+8.2251	+8.2778	+8.3305	+8.3833	+8.4360
+290	+5.5100	+8.2650	+8.3201	+8.3752	+8.4303	+8.4854	+8.5405	+8.5956	+8.6507	+8.7058	+8.7609	+8.8160
+295	+5.7525	+8.6287	+8.6863	+8.7438	+8.8013	+8.8588	+8.9164	+8.9739	+9.0314	+9.0889	+9.1465	+9.2040
+300	+6.0000	+9.0000	+9.0600	+9.1200	+9.1800	+9.2400	+9.3000	+9.3600	+9.4200	+9.4800	+9.5400	+9.6000
+305	+6.2525	+9.3787	+9.4413	+9.5038	+9.5663	+9.6288	+9.6914	+9.7539	+9.8164	+9.8789	+9.9415	+10.0040
+310	+6.5100	+9.7650	+9.8301	+9.8952	+9.9603	+10.0254	+10.0905	+10.1556	+10.2207	+10.2858	+10.3509	+10.4160
+315	+6.7725	+10.1587	+10.2265	+10.2942	+10.3619	+10.4296	+10.4974	+10.5651	+10.6328	+10.7005	+10.7683	+10.8360
+320	+7.0400	+10.5600	+10.6304	+10.7008	+10.7712	+10.8415	+10.9120	+10.9824	+11.0528	+11.1232	+11.1936	+11.2640
+325	+7.3125	+10.9687	+11.0419	+11.1150	+11.1881	+11.2612	+11.3344	+11.4075	+11.4806	+11.5537	+11.6269	+11.7000
+330	+7.5900	+11.3850	+11.4609	+11.5368	+11.6127	+11.6886	+11.7645	+11.8404	+11.9163	+11.9922	+12.0681	+12.1440

APPENDIX TABLE I. (continued).—To find d for given values of T and δ . Deduced from the formula $d = \delta \left[\left(\frac{T}{100} \right)^2 - \frac{T}{100} \right]$.

T.	$\left(\frac{t}{100} \right)^2 - \frac{t}{100}$	$\delta = 1.500.$	$\delta = 1.510.$	$\delta = 1.520.$	$\delta = 1.530.$	$\delta = 1.540.$	$\delta = 1.550.$	$\delta = 1.560.$	$\delta = 1.570.$	$\delta = 1.580.$	$\delta = 1.590.$	$\delta = 1.600.$
+335	+7.8725	+11.8087	+11.8875	+11.9662	+12.0449	+12.1236	+12.2024	+12.2811	+12.3598	+12.4385	+12.5173	+12.5960
+340	+8.1600	+12.2400	+12.3216	+12.4032	+12.4848	+12.5664	+12.6480	+12.7296	+12.8112	+12.8928	+12.9744	+13.0560
+345	+8.4525	+12.6787	+12.7633	+12.8478	+12.9323	+13.0168	+13.1014	+13.1859	+13.2704	+13.3549	+13.4395	+13.5240
+350	+8.7500	+13.1250	+13.2125	+13.3000	+13.3875	+13.4750	+13.5625	+13.6500	+13.7375	+13.8250	+13.9125	+14.0000
+355	+9.0525	+13.5787	+13.6693	+13.7598	+13.8503	+13.9408	+14.0314	+14.1219	+14.2124	+14.3029	+14.3935	+14.4840
+360	+9.3600	+14.0400	+14.1336	+14.2272	+14.3208	+14.4144	+14.5080	+14.6016	+14.6952	+14.7888	+14.8824	+14.9760
+365	+9.6725	+14.5087	+14.6055	+14.7022	+14.7989	+14.8956	+14.9924	+15.0891	+15.1858	+15.2825	+15.3793	+15.4760
+370	+9.9900	+14.9850	+15.0849	+15.1848	+15.2847	+15.3846	+15.4845	+15.5844	+15.6843	+15.7842	+15.8841	+15.9840
+375	+10.3125	+15.4687	+15.5719	+15.6750	+15.7781	+15.8812	+15.9844	+16.0875	+16.1906	+16.2937	+16.3969	+16.5000
+380	+10.6400	+15.9600	+16.0664	+16.1728	+16.2792	+16.3856	+16.4920	+16.5984	+16.7048	+16.8112	+16.9176	+17.0240
+385	+10.9725	+16.4587	+16.5685	+16.6782	+16.7879	+16.8976	+17.0074	+17.1171	+17.2268	+17.3365	+17.4463	+17.5560
+390	+11.3100	+16.9650	+17.0781	+17.1912	+17.3043	+17.4174	+17.5305	+17.6436	+17.7567	+17.8698	+17.9829	+18.0960
+395	+11.6525	+17.4787	+17.5953	+17.7118	+17.8283	+17.9448	+18.0614	+18.1779	+18.2944	+18.4109	+18.5275	+18.6440
+400	+12.0000	+18.0000	+18.1200	+18.2400	+18.3600	+18.4800	+18.6000	+18.7200	+18.8400	+18.9600	+19.0800	+19.2000
+405	+12.3525	+18.5287	+18.6523	+18.7758	+18.8993	+19.0228	+19.1464	+19.2699	+19.3934	+19.5169	+19.6405	+19.7640
+410	+12.7100	+19.0650	+19.1921	+19.3192	+19.4463	+19.5734	+19.7005	+19.8276	+19.9547	+20.0818	+20.2089	+20.3360
+415	+13.0725	+19.6087	+19.7395	+19.8702	+20.0009	+20.1316	+20.2624	+20.3931	+20.5238	+20.6545	+20.7853	+20.9160
+420	+13.4400	+20.1600	+20.2944	+20.4288	+20.5632	+20.6976	+20.8320	+20.9664	+21.1008	+21.2352	+21.3696	+21.5040
+425	+13.8125	+20.7187	+20.8569	+20.9950	+21.1331	+21.2712	+21.4094	+21.5475	+21.6856	+21.8237	+21.9619	+22.1000
+430	+14.1900	+21.2850	+21.4269	+21.5688	+21.7107	+21.8526	+21.9945	+22.1364	+22.2783	+22.4202	+22.5621	+22.7040
+435	+14.5725	+21.8587	+22.0045	+22.1502	+22.2959	+22.4416	+22.5874	+22.7331	+22.8788	+23.0245	+23.1703	+23.3160
+440	+14.9600	+22.4400	+22.5896	+22.7392	+22.8888	+23.0384	+23.1880	+23.3376	+23.4872	+23.6368	+23.7864	+23.9360
+444.53	+15.3154	+22.9731	+23.1262	+23.2794	+23.4325	+23.5857	+23.7389	+23.8920	+24.0452	+24.1983	+24.3515	+24.5046
+445	+15.3525	+23.0287	+23.1823	+23.3358	+23.4893	+23.6428	+23.7964	+23.9499	+24.1034	+24.2569	+24.4105	+24.5640
+445.27	+15.3738	+23.0607	+23.2144	+23.3682	+23.5219	+23.6756	+23.8294	+23.9831	+24.1369	+24.2906	+24.4443	+24.5981
+450	+15.7500	+23.6250	+23.7825	+23.9400	+24.0975	+24.2550	+24.4125	+24.5700	+24.7275	+24.8850	+25.0425	+25.2000
+455	+16.1525	+24.2287	+24.3903	+24.5518	+24.7133	+24.8748	+25.0364	+25.1979	+25.3594	+25.5209	+25.6825	+25.8440
+460	+16.5600	+24.8400	+25.0056	+25.1712	+25.3368	+25.5024	+25.6680	+25.8336	+25.9992	+26.1648	+26.3304	+26.4960

APPENDIX TABLE II.—For calculating T when pt and δ are known, employing the

$$\text{formula } T = \left(\frac{5000}{\delta} + 50 \right) - \sqrt{\left(\frac{5000}{\delta} + 50 \right)^2 - \frac{10000pt}{\delta}}.$$

$pt.$	T.					
	$\delta = 1.54.$	$\delta = 1.55.$	$\delta = 1.56.$	$\delta = 1.57.$		
-50	-48.879	-48.872	-48.865	-48.858	970	
-49	-47.909	-47.902	-47.895	-47.888	1	97
-48	-46.938	-46.931	-46.925	-46.918	2	194
-47	-45.967	-45.960	-45.954	-45.948	3	291
-46	-44.996	-44.989	-44.983	-44.977	4	388
-45	-44.024	-44.018	-44.012	-44.006	5	485
-44	-43.052	-43.046	-43.040	-43.034	6	582
-43	-42.079	-42.074	-42.068	-42.062	7	679
-42	-41.106	-41.101	-41.096	-41.090	8	776
-41	-40.133	-40.128	-40.123	-40.118	9	873
-40	-39.160	-39.155	-39.150	-39.145		
-39	-38.187	-38.182	-38.177	-38.172		
-38	-37.214	-37.209	-37.204	-37.199		
-37	-36.240	-36.235	-36.230	-36.225		
-36	-35.266	-35.261	-35.256	-35.251		
-35	-34.291	-34.287	-34.282	-34.277		
-34	-33.316	-33.312	-33.308	-33.303		
-33	-32.341	-32.337	-32.333	-32.329		
-32	-31.366	-31.362	-31.358	-31.354		
-31	-30.390	-30.386	-30.382	-30.378		
-30	-29.414	-29.410	-29.406	-29.402		
-29	-28.438	-28.434	-28.430	-28.426		
-28	-27.461	-27.458	-27.454	-27.450		
-27	-26.484	-26.481	-26.478	-26.474		
-26	-25.507	-25.504	-25.501	-25.498		
-25	-24.530	-24.527	-24.524	-24.521		
-24	-23.552	-23.549	-23.546	-23.544		
-23	-22.574	-22.571	-22.568	-22.566		
-22	-21.596	-21.593	-21.590	-21.588		
-21	-20.617	-20.615	-20.612	-20.610		
-20	-19.638	-19.636	-19.634	-19.632		
-19	-18.659	-18.657	-18.655	-18.653		
-18	-17.680	-17.678	-17.676	-17.674		
-17	-16.700	-16.698	-16.697	-16.695	980	
-16	-15.720	-15.718	-15.717	-15.716	1	98
-15	-14.740	-14.738	-14.737	-14.736	2	196
-14	-13.759	-13.758	-13.757	-13.756	3	294
-13	-12.778	-12.777	-12.776	-12.775	4	392
-12	-11.797	-11.796	-11.795	-11.794	5	490
-11	-10.816	-10.815	-10.814	-10.813	6	588
-10	-9.834	-9.833	-9.832	-9.831	7	686
-9	-8.852	-8.851	-8.850	-8.849	8	784
-8	-7.870	-7.869	-7.868	-7.867	9	882
-7	-6.887	-6.886	-6.886	-6.885		
-6	-5.904	-5.903	-5.903	-5.903		
-5	-4.921	-4.920	-4.920	-4.920		
-4	-3.937	-3.937	-3.937	-3.937		
-3	-2.953	-2.953	-2.953	-2.953		
-2	-1.969	-1.969	-1.969	-1.969		
-1	-0.985	-0.985	-0.985	-0.985		

APPENDIX TABLE II. (continued).—For calculating T when pt and δ are known,employing the formula $T = \left(\frac{5000}{\delta} + 50\right) - \sqrt{\left(\frac{5000}{\delta} + 50\right)^2 - \frac{10000pt}{\delta}}$.

pt	T .					
	$\delta = 1.54.$	$\delta = 1.55.$	$\delta = 1.56.$	$\delta = 1.57.$		
0	0.000	0.000	0.000	0.000		
1	0.985	0.985	0.985	0.985		
2	1.970	1.970	1.970	1.970		
3	2.955	2.955	2.955	2.955		
4	3.941	3.941	3.941	3.941		
5	4.927	4.927	4.927	4.927		
6	5.914	5.913	5.913	5.913		
7	6.901	6.900	6.899	6.899		
8	7.888	7.887	7.886	7.885		
9	8.875	8.874	8.873	8.872		
10	9.863	9.862	9.861	9.860		
11	10.851	10.850	10.849	10.848		
12	11.839	11.838	11.837	11.836		
13	12.827	12.826	12.825	12.824		
14	13.816	13.815	13.814	13.813		
15	14.805	14.804	14.803	14.802		
16	15.795	15.794	15.792	15.791		
17	16.785	16.784	16.782	16.780		
18	17.775	17.774	17.772	17.770		
19	18.765	18.764	18.762	18.760		
20	19.756	19.754	19.752	19.751		
21	20.747	20.745	20.743	20.741		
22	21.738	21.736	21.734	21.732		
23	22.730	22.728	22.726	22.724		
24	23.722	23.720	23.718	23.716		
25	24.714	24.712	24.710	24.708		
26	25.706	25.704	25.702	25.700		
27	26.699	26.697	26.695	26.693		
28	27.692	27.690	27.688	27.686		
29	28.685	28.683	28.681	28.679		
30	29.679	29.677	29.675	29.673		
31	30.673	30.671	30.669	30.667		
32	31.667	31.665	31.663	31.661		
33	32.661	32.659	32.657	32.655		
34	33.656	33.654	33.652	33.650		
35	34.651	34.649	34.647	34.645		
36	35.646	35.644	35.642	35.640		
37	36.642	36.640	36.638	36.636		
38	37.638	37.636	37.634	37.632		
39	38.634	38.632	38.630	38.628		
40	39.631	39.629	39.627	39.625		
41	40.628	40.626	40.624	40.622		
42	41.625	41.623	41.621	41.619		
43	42.623	42.621	42.619	42.617		
44	43.621	43.619	43.617	43.615		
45	44.619	44.617	44.615	44.613		
46	45.617	45.615	45.613	45.611		
47	46.616	46.614	46.612	46.610		
48	47.615	47.613	47.611	47.609		
49	48.615	48.613	48.611	48.609		

990

1	99
2	198
3	297
4	396
5	495
6	594
7	693
8	792
9	891

1000

1	100
2	200
3	300
4	400
5	500
6	600
7	700
8	800
9	900

APPENDIX TABLE II. (continued).—For calculating T when pt and δ are known, employing the formula $T = \left(\frac{5000}{\delta} + 50\right) - \sqrt{\left(\frac{5000}{\delta} + 50\right)^2 - \frac{10000pt}{\delta}}$.

pt .	T .					
	$\delta = 1.54$.	$\delta = 1.55$.	$\delta = 1.56$.	$\delta = 1.57$.		
50	49.615	49.613	49.611	49.609	1000	
51	50.615	50.613	50.611	50.609	1	100
52	51.615	51.613	51.611	51.609	2	200
53	52.616	52.614	52.612	52.610	3	300
54	53.617	53.615	53.613	53.611	4	400
55	54.619	54.617	54.615	54.613	5	500
56	55.621	55.619	55.617	55.615	6	600
57	56.623	56.621	56.619	56.617	7	700
58	57.625	57.623	57.621	57.619	8	800
59	58.627	58.625	58.623	58.621	9	900
60	59.630	59.627	59.625	59.623		
61	60.633	60.630	60.628	60.626		
62	61.636	61.633	61.631	61.629		
63	62.639	62.637	62.635	62.633		
64	63.643	63.641	63.639	63.637		
65	64.648	64.646	64.644	64.642		
66	65.653	65.651	65.649	65.647		
67	66.658	66.656	66.654	66.652		
68	67.663	67.661	67.659	67.657		
69	68.669	68.667	68.665	68.663		
70	69.675	69.673	69.671	69.669		
71	70.681	70.679	70.677	70.675		
72	71.687	71.685	71.683	71.681		
73	72.694	72.692	72.690	72.688		
74	73.701	73.699	73.697	73.695		
75	74.709	74.707	74.705	74.703		
76	75.717	75.715	75.713	75.711		
77	76.725	76.723	76.721	76.719		
78	77.734	77.732	77.730	77.728		
79	78.743	78.741	78.739	78.737		
80	79.752	79.750	79.748	79.746		
81	80.761	80.759	80.757	80.755	1010	
82	81.771	81.769	81.767	81.765	1	101
83	82.781	82.779	82.777	82.775	2	202
84	83.791	83.789	83.787	83.785	3	303
85	84.801	84.800	84.798	84.796	4	404
86	85.812	85.811	85.809	85.808	5	505
87	86.823	86.822	86.821	86.820	6	606
88	87.835	87.834	87.833	87.832	7	707
89	88.847	88.846	88.845	88.844	8	808
90	89.859	89.858	89.857	89.856	9	909
91	90.872	90.871	90.870	90.869		
92	91.885	91.884	91.883	91.882		
93	92.898	92.897	92.896	92.895		
94	93.912	93.911	93.910	93.909		
95	94.926	94.925	94.924	94.924		
96	95.940	95.939	95.939	95.939		
97	96.954	96.954	96.954	96.954		
98	97.969	97.969	97.969	97.969		
99	98.984	98.984	98.984	98.984		

APPENDIX TABLE II. (continued).—For calculating T when pt and δ are known, employing the formula $T = \left(\frac{5000}{\delta} + 50\right) - \sqrt{\left(\frac{5000}{\delta} + 50\right)^2 - \frac{10000pt}{\delta}}$.

$pt.$	$T.$					
	$\delta = 1.54$	$\delta = 1.55$	$\delta = 1.56$	$\delta = 1.57$		
100	100.000	100.000	100.000	100.000		
101	101.016	101.016	101.016	101.016		
102	102.032	102.032	102.032	102.032		
103	103.048	103.049	103.049	103.049		
104	104.065	104.066	104.066	104.066		
105	105.082	105.083	105.083	105.084		
106	106.099	106.100	106.101	106.102		
107	107.117	107.118	107.119	107.120		
108	108.135	108.136	108.137	108.138		
109	109.154	109.155	109.156	109.157		
110	110.173	110.174	110.175	110.176		
111	111.192	111.193	111.194	111.195		
112	112.211	112.212	112.214	112.214	1020	
113	113.230	113.232	113.234	113.235	1	102
114	114.250	114.252	114.254	114.256	2	204
115	115.271	115.273	115.275	115.277	3	306
116	116.292	116.294	116.296	116.298	4	408
117	117.313	117.315	117.317	117.320	5	510
118	118.334	118.336	118.339	118.342	6	612
119	119.355	119.358	119.361	119.364	7	714
120	120.377	120.380	120.383	120.386	8	816
121	121.400	121.403	121.406	121.409	9	918
122	122.423	122.426	122.429	122.432		
123	123.446	123.449	123.452	123.455		
124	124.469	124.472	124.476	124.478		
125	125.492	125.496	125.500	125.502		
126	126.516	126.520	126.524	126.526		
127	127.540	127.544	127.548	127.551		
128	128.565	128.569	128.573	128.576		
129	129.590	129.594	129.598	129.602		
130	130.616	130.620	130.624	130.628		
131	131.642	131.646	131.650	131.654		
132	132.668	132.672	132.676	132.680		
133	133.694	133.698	133.703	133.707		
134	134.720	134.725	134.730	134.734		
135	135.747	135.752	135.757	135.762		
136	136.774	136.780	136.785	136.790		
137	137.802	137.808	137.813	137.818		
138	138.830	138.836	138.841	138.846		
139	139.858	139.864	139.870	139.875	1030	
140	140.887	140.893	140.899	140.904		
141	141.916	141.922	141.928	141.934	1	103
142	142.945	142.952	142.957	142.964	2	206
143	143.975	143.982	143.987	143.994	3	309
144	145.005	145.012	145.017	145.025	4	412
145	146.035	146.042	146.048	146.056	5	515
146	147.066	147.073	147.079	147.087	6	618
147	148.097	148.104	148.111	148.118	7	721
148	149.128	149.136	149.143	149.150	8	824
149	150.160	150.168	150.175	150.183	9	927

APPENDIX TABLE II. (continued).—For calculating T when pt and δ are known,employing the formula $T = \left(\frac{5000}{\delta} + 50\right) - \sqrt{\left(\frac{5000}{\delta} + 50\right)^2 - \frac{10000pt}{\delta}}$.

pt .	T .				
	$\delta = 1.54$.	$\delta = 1.55$.	$\delta = 1.56$.	$\delta = 1.57$.	
150	151.192	151.200	151.208	151.216	
151	152.224	152.232	152.241	152.249	
152	153.257	153.265	153.274	153.282	
153	154.290	154.299	154.308	154.316	
154	155.324	155.333	155.342	155.350	
155	156.358	156.367	156.376	156.384	
156	157.392	157.401	157.410	157.418	
157	158.426	158.435	158.444	158.453	
158	159.460	159.470	159.479	159.488	
159	160.495	160.505	160.515	160.524	
160	161.531	161.541	161.551	161.560	
161	162.567	162.577	162.587	162.597	
162	163.603	163.613	163.623	163.634	
163	164.639	164.650	164.660	164.672	
164	165.676	165.687	165.697	165.710	
165	166.713	166.724	166.735	166.748	
166	167.750	167.762	167.773	167.786	
167	168.788	168.800	168.811	168.824	
168	169.826	169.838	169.850	169.862	
169	170.864	170.877	170.889	170.901	
170	171.903	171.916	171.929	171.940	
171	172.942	172.956	172.969	172.980	
172	173.982	173.996	174.009	174.021	
173	175.022	175.036	175.049	175.063	
174	176.062	176.076	176.090	176.105	
175	177.102	177.117	177.131	177.147	
176	178.143	178.158	178.173	178.189	
177	179.185	179.200	179.215	179.231	
178	180.227	180.242	180.257	180.273	
179	181.269	181.284	181.300	181.316	
180	182.311	182.327	182.343	182.359	
181	183.353	183.370	183.386	183.403	
182	184.396	184.413	184.430	184.447	
183	185.440	185.457	185.474	185.491	
184	186.484	186.501	186.518	186.536	
185	187.528	187.545	187.563	187.581	
186	188.572	188.590	188.608	188.626	
187	189.617	189.635	189.653	189.671	
188	190.662	190.680	190.698	190.716	
189	191.707	191.726	191.744	191.763	
190	192.753	192.772	192.790	192.810	
191	193.799	193.818	193.837	193.857	
192	194.845	194.865	194.884	194.904	
193	195.892	195.912	195.932	195.952	
194	196.939	196.960	196.980	197.000	
195	197.987	198.008	198.028	198.049	
196	199.035	199.056	199.077	199.098	
197	200.084	200.105	200.126	200.147	
198	201.133	201.154	201.175	201.196	
199	202.182	202.203	202.225	202.246	

1040	
1	104
2	208
3	312
4	416
5	520
6	624
7	728
8	832
9	936

APPENDIX TABLE II. (continued).—For calculating T when pt and δ are known,employing the formula $T = \left(\frac{5000}{\delta} + 50\right) - \sqrt{\left(\frac{5000}{\delta} + 50\right)^2 - \frac{10000pt}{\delta}}$.

$pt.$	$T.$					
	$\delta = 1.54.$	$\delta = 1.55.$	$\delta = 1.56.$	$\delta = 1.57.$		
200	203.231	203.253	203.275	203.296	1050	
201	204.281	204.303	204.325	204.347	1	105
202	205.331	205.353	205.376	205.399	2	210
203	206.381	206.404	206.427	206.451	3	315
204	207.431	207.455	207.479	207.503	4	420
205	208.482	208.507	208.531	208.555	5	525
206	209.534	209.559	209.583	209.607	6	630
207	210.586	210.611	210.635	210.659	7	735
208	211.638	211.663	211.688	211.712	8	840
209	212.690	212.716	212.742	212.766	9	945
210	213.743	213.769	213.796	213.820		
211	214.796	214.823	214.850	214.875		
212	215.850	215.877	215.904	215.930		
213	216.904	216.931	216.958	216.985		
214	217.958	217.986	218.013	218.041		
215	219.013	219.041	219.069	219.097		
216	220.068	220.097	220.125	220.153		
217	221.124	221.153	221.182	221.210		
218	222.180	222.209	222.239	222.267		
219	223.236	223.266	223.296	223.325		
220	224.293	224.323	224.353	224.383		
221	225.350	225.380	225.410	225.441		
222	226.407	226.438	226.468	226.499		
223	227.464	227.496	227.527	227.557		
224	228.522	228.554	228.586	228.616		
225	229.581	229.613	229.645	229.676		
226	230.640	230.672	230.704	230.736		
227	231.699	231.731	231.764	231.797	1060	
228	232.758	232.791	232.824	232.858	1	106
229	233.817	233.851	233.885	233.919	2	212
230	234.877	234.912	234.946	234.980	3	318
231	235.938	235.973	236.007	236.041	4	424
232	236.999	237.035	237.069	237.103	5	530
233	238.061	238.097	238.131	238.165	6	636
234	239.123	239.159	239.194	239.228	7	742
235	240.185	240.221	240.257	240.291	8	848
236	241.248	241.284	241.320	241.355	9	954
237	242.311	242.347	242.384	242.420		
238	243.374	243.411	243.448	243.485		
239	244.437	244.475	244.512	244.550		
240	245.501	245.539	245.577	245.615		
241	246.565	246.604	246.642	246.680		
242	247.630	247.669	247.707	247.746		
243	248.695	248.734	248.773	248.812		
244	249.760	249.800	249.839	249.879		
245	250.826	250.866	250.906	250.946		
246	251.892	251.933	251.973	252.014		
247	252.958	253.000	253.041	253.082		
248	254.025	254.067	254.109	254.150		
249	255.092	255.135	255.177	255.219		

APPENDIX TABLE II. (continued).—For calculating T when pt and δ are known, employing the formula $T = \left(\frac{5000}{\delta} + 50\right) - \sqrt{\left(\frac{5000}{\delta} + 50\right)^2 - \frac{10000pt}{\delta}}$

$pt.$	$T.$				
	$\delta = 1.54.$	$\delta = 1.55.$	$\delta = 1.56.$	$\delta = 1.57.$	
250	256.160	256.203	256.245	256.288	1070
251	257.228	257.271	257.314	257.357	
252	258.296	258.340	258.383	258.427	
253	259.365	259.409	259.453	259.497	
254	260.434	260.479	260.523	260.568	
255	261.504	261.549	261.594	261.639	
256	262.574	262.620	262.665	262.711	
257	263.644	263.691	263.737	263.783	
258	264.715	264.762	264.809	264.855	
259	265.786	265.833	265.881	265.928	
260	266.857	266.905	266.953	267.001	1080
261	267.929	267.977	268.025	268.074	
262	269.001	269.050	269.098	269.148	
263	270.073	270.123	270.172	270.222	
264	271.146	271.196	271.246	271.296	
265	272.219	272.270	272.320	272.370	
266	273.293	273.344	273.395	273.445	
267	274.367	274.419	274.470	274.521	
268	275.442	275.494	275.545	275.597	
269	276.517	276.569	276.621	276.673	
270	277.592	277.645	277.698	277.750	1090
271	278.667	278.721	278.775	278.827	
272	279.743	279.798	279.852	279.905	
273	280.820	280.875	280.930	280.984	
274	281.897	281.952	282.008	282.063	
275	282.974	283.029	283.086	283.142	
276	284.052	284.107	284.164	284.221	
277	285.130	285.186	285.243	285.300	
278	286.209	286.265	286.323	286.380	
279	287.288	287.344	287.403	287.460	
280	288.367	288.424	288.483	288.541	1100
281	289.446	289.504	289.563	289.622	
282	290.525	290.584	290.644	290.704	
283	291.605	291.665	291.726	291.786	
284	292.685	292.746	292.808	292.868	
285	293.766	293.827	293.890	293.951	
286	294.847	294.909	294.972	295.034	
287	295.929	295.992	296.055	296.117	
288	297.012	297.075	297.139	297.201	
289	298.095	298.158	298.223	298.286	
290	299.178	299.241	299.307	299.371	1110
291	300.261	300.325	300.391	300.456	
292	301.344	301.409	301.476	301.541	
293	302.428	302.494	302.561	302.627	
294	303.512	303.579	303.646	303.713	
295	304.597	304.665	304.732	304.800	
296	305.682	305.751	305.819	305.887	
297	306.768	306.837	306.906	306.975	
298	307.854	307.924	307.993	308.063	
299	308.940	309.011	309.080	309.151	

APPENDIX TABLE II. (continued).—For calculating T when pt and δ are known,employing the formula $T = \left(\frac{5000}{\delta} + 50\right) - \sqrt{\left(\frac{5000}{\delta} + 50\right)^2 - \frac{10000pt}{\delta}}$.

pt	T					
	$\delta = 1.54.$	$\delta = 1.55.$	$\delta = 1.56.$	$\delta = 1.57.$		
300	310.027	310.098	310.168	310.240		
301	311.115	311.186	311.257	311.329		
302	312.203	312.274	312.346	312.419		
303	313.290	313.363	313.435	313.509		
304	314.379	314.452	314.525	314.599		
305	315.468	315.542	315.616	315.690		
306	316.557	316.632	316.707	316.781		
307	317.647	317.722	317.798	317.873		
308	318.737	318.813	318.889	318.965		
309	319.827	319.904	319.980	320.057		
310	320.918	320.995	321.072	321.150		
311	322.010	322.087	322.165	322.243		
312	323.102	323.180	323.258	323.337		
313	324.194	324.273	324.352	324.432		
314	325.286	325.366	325.446	325.527		
315	326.379	326.459	326.540	326.622		
316	327.472	327.553	327.634	327.717		
317	328.565	328.647	328.729	328.812		
318	329.659	329.742	329.824	329.908		
319	330.754	330.837	330.920	331.004		
320	331.849	331.933	332.017	332.101		
321	332.944	333.029	333.114	333.199		
322	334.039	334.125	334.211	334.297		
323	335.135	335.222	335.308	335.395		
324	336.232	336.319	336.406	336.494		
325	337.329	337.417	337.505	337.593		
326	338.426	338.515	338.604	338.693		
327	339.524	339.613	339.703	339.793		
328	340.622	340.712	340.802	340.893		
329	341.720	341.811	341.902	341.993		
330	342.819	342.911	343.003	343.094		
331	343.918	344.011	344.104	344.196		
332	345.018	345.112	345.205	345.298		
333	346.119	346.213	346.307	346.401		
334	347.220	347.314	347.409	347.504		
335	348.321	348.416	348.511	348.607		
336	349.422	349.518	349.614	349.710		
337	350.523	350.620	350.717	350.814		
338	351.625	351.723	351.820	351.918		
339	352.728	352.826	352.924	353.022		
340	353.831	353.930	354.029	354.127		
341	354.934	355.034	355.134	355.233		
342	356.038	356.139	356.239	356.340		
343	357.143	357.244	357.345	357.447		
344	358.248	358.350	358.452	358.554		
345	359.353	359.456	359.559	359.662		
346	360.458	360.562	360.666	360.770		
347	361.564	361.668	361.773	361.878		
348	362.670	362.775	362.880	362.986		
349	363.777	363.883	363.988	364.095		

1090

1	109
2	218
3	327
4	436
5	545
6	654
7	763
8	872
9	981

1100

1	110
2	220
3	330
4	440
5	550
6	660
7	770
8	880
9	990

APPENDIX TABLE II. (continued).—For calculating T when pt and δ are known, employing the formula $T = \left(\frac{5000}{\delta} + 50\right) - \sqrt{\left(\frac{5000}{\delta} + 50\right)^2 - \frac{10000pt}{\delta}}$.

$pt.$	$T.$					
	$\delta = 1.54.$	$\delta = 1.55.$	$\delta = 1.56.$	$\delta = 1.57.$		
350	364.884	364.991	365.097	365.205		
351	365.992	366.100	366.207	366.316		
352	367.100	367.209	367.317	367.427		
353	368.208	368.318	368.427	368.538		
354	369.317	369.428	369.538	369.649		
355	370.426	370.538	370.649	370.760		
356	371.536	371.648	371.760	371.871		
357	372.647	372.759	372.871	372.983		
358	373.758	373.871	373.984	374.097		
359	374.869	374.983	375.097	375.211		
360	375.980	376.095	376.210	376.325		
361	377.092	377.208	377.324	377.440		
362	378.204	378.321	378.438	378.555		
363	379.316	379.434	379.552	379.670		
364	380.429	380.548	380.666	380.785		
365	381.543	381.662	381.781	381.900		
366	382.657	382.777	382.897	383.017		
367	383.772	383.892	384.013	384.134		
368	384.887	385.008	385.129	385.251		
369	386.002	386.124	386.246	386.369		
370	387.118	387.241	387.364	387.488		
371	388.234	388.358	388.482	388.607		
372	389.350	389.475	389.600	389.726		
373	390.467	390.593	390.719	390.845		
374	391.584	391.711	391.838	391.965		
375	392.702	392.830	392.958	393.086		
376	393.820	393.949	394.078	394.207		
377	394.939	395.069	395.199	395.329		
378	396.058	396.189	396.320	396.451		
379	397.177	397.309	397.441	397.573		
380	398.297	398.430	398.563	398.696		
381	399.417	399.551	399.685	399.819		
382	400.538	400.673	400.808	400.943		
383	401.659	401.795	401.931	402.067		
384	402.781	402.918	403.055	403.192		
385	403.903	404.041	404.179	404.317		
386	405.026	405.165	405.304	405.443		
387	406.149	406.289	406.429	406.569		
388	407.272	407.413	407.554	407.695		
389	408.396	408.538	408.679	408.822		
390	409.521	409.663	409.805	409.949		
391	410.646	410.789	410.932	411.076		
392	411.771	411.915	412.060	412.204		
393	412.896	413.041	413.187	413.333		
394	414.021	414.168	414.315	414.462		
395	415.148	415.296	415.444	415.592		
396	416.275	416.424	416.573	416.722		
397	417.402	417.552	417.702	417.852		
398	418.530	418.681	418.832	418.983		
399	419.658	419.810	419.962	420.114		

1110

1	111
2	222
3	333
4	444
5	555
6	666
7	777
8	888
9	999

1120

1	112
2	224
3	336
4	448
5	560
6	672
7	784
8	896
9	1008

APPENDIX TABLE II. (continued).—For calculating T when pt and δ are known,employing the formula $T = \left(\frac{5000}{\delta} + 50\right) - \sqrt{\left(\frac{5000}{\delta} + 50\right)^2 - \frac{10000pt}{\delta}}$.

pt .	T .					
	$\delta = 1.54$.	$\delta = 1.55$.	$\delta = 1.56$.	$\delta = 1.57$.		
400	420.787	420.940	421.093	421.246	1130	
401	421.916	422.070	422.224	422.378	1	113
402	423.046	423.201	423.356	423.511	2	226
403	424.176	424.332	424.488	424.644	3	339
404	425.306	425.463	425.620	425.777	4	452
405	426.437	426.595	426.753	426.911	5	565
406	427.569	427.728	427.887	428.046	6	678
407	428.701	428.861	429.021	429.181	7	791
408	429.833	429.994	430.055	430.216	8	904
409	430.966	431.128	431.290	431.452	9	1017
410	432.099	432.262	432.425	432.588		
411	433.233	433.397	433.561	433.725		
412	434.367	434.532	434.697	434.862		
413	435.501	435.667	435.833	435.999		
414	436.636	436.803	436.970	437.137		
415	437.772	437.940	438.108	438.276		
416	438.908	439.077	439.246	439.416		
417	440.044	440.214	440.385	440.556		
418	441.181	441.352	441.524	441.696		
419	442.318	442.490	442.663	442.836		
420	443.456	443.629	443.803	443.977		
421	444.594	444.768	444.943	445.118		
422	445.733	445.908	446.084	446.260	1140	
423	446.872	447.048	447.225	447.402	1	114
424	448.011	448.188	448.366	448.544	2	228
425	449.151	449.329	449.508	449.687	3	342
426	450.291	450.471	450.650	450.831	4	456
427	451.432	451.613	451.794	451.976	5	570
428	452.573	452.755	452.938	453.121	6	684
429	453.715	453.898	454.082	454.266	7	798
430	454.858	455.042	455.227	455.412	8	912
431	456.001	456.186	456.372	456.558	9	1026
432	457.144	457.330	457.517	457.704		
433	458.287	458.475	458.663	458.851		
434	459.431	459.620	459.810	459.999		
435	460.576	460.766	460.957	461.147		
436	461.721	461.912	462.104	462.296		
437	462.866	463.058	463.252	463.445		
438	464.011	464.205	464.400	464.595		
439	465.158	465.353	465.549	465.745	1150	
440	466.305	466.501	466.698	466.895	1	115
441	467.452	467.649	467.847	468.045	2	230
442	468.600	468.798	468.997	469.196	3	345
443	469.748	469.948	470.148	470.348	4	460
444	470.897	471.098	471.299	471.500	5	575
445	472.046	472.248	472.451	472.653	6	690
446	473.196	473.399	473.603	473.807	7	805
447	474.346	474.550	474.756	474.961	8	920
448	475.496	475.702	475.909	476.115	9	1035
449	476.647	476.854	477.062	477.270		

APPENDIX TABLE II. (continued).—For calculating T when pt and δ are known,employing the formula $T = \left(\frac{5000}{\delta} + 50\right) - \sqrt{\left(\frac{5000}{\delta} + 50\right)^2 - \frac{10000pt}{\delta}}$.

$pt.$	T.				
	$\delta = 1.54.$	$\delta = 1.55.$	$\delta = 1.56.$	$\delta = 1.57.$	
450	477.799	478.007	478.216	478.425	1150
451	478.951	479.160	479.370	479.580	
452	480.103	480.314	480.525	480.736	
453	481.256	481.468	481.680	481.893	
454	482.410	482.623	482.836	483.050	
455	483.564	483.778	483.992	484.207	
456	484.718	484.933	485.149	485.365	
457	485.873	486.089	486.306	486.524	
458	487.028	487.246	487.464	487.683	
459	488.184	488.403	488.622	488.842	1150
460	489.341	489.561	489.781	490.002	
461	490.498	490.719	490.940	491.162	
462	491.655	491.877	492.100	492.323	
463	492.812	493.036	493.260	493.485	
464	493.969	494.195	494.421	494.647	
465	495.127	495.355	495.582	495.810	
466	496.286	496.516	496.744	496.973	
467	497.446	497.677	497.907	498.137	1160
468	498.606	498.838	499.070	499.301	
469	499.766	500.000	500.233	500.465	
470	500.927	501.162	501.396	501.630	
471	502.089	502.325	502.560	502.796	
472	503.251	503.488	503.725	503.962	
473	504.414	504.652	504.890	505.128	
474	505.577	505.816	506.055	506.295	
475	506.741	506.981	507.221	507.462	1170
476	507.905	508.147	508.388	508.630	
477	509.070	509.313	509.555	509.799	
478	510.235	510.479	510.723	510.968	
479	511.400	511.646	511.891	512.138	
480	512.565	512.812	513.060	513.308	
481	513.731	513.981	514.229	514.478	
482	514.898	515.149	515.399	515.649	
483	516.065	516.318	516.569	516.821	1170
484	517.233	517.487	517.740	517.993	
485	518.402	518.657	518.911	519.165	
486	519.571	519.827	520.082	520.338	
487	520.741	520.998	521.254	521.512	
488	521.911	522.169	522.427	522.686	
489	523.081	523.340	523.600	523.861	
490	524.251	524.512	524.773	525.036	
491	525.422	525.685	525.947	526.211	1170
492	526.594	526.858	527.122	527.387	
493	527.766	528.032	528.297	528.563	
494	528.938	529.206	529.473	529.740	
495	530.111	530.381	530.649	530.917	
496	531.285	531.556	531.825	532.095	
497	532.460	532.732	533.002	533.274	
498	533.635	533.908	534.179	534.453	
499	534.811	535.085	535.358	535.633	1170
500	535.987	536.262	536.537	536.813	

APPENDIX TABLE III.—Temperatures of Ebullition of Water under varying Pressures.
Calculated by Dr. BROCH from the observations of REGNAULT.

Millims.	Tenths of a millimetre										Pro. Pts.
	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.	
730	98°·8802	·8840	·8878	·8916	·8954	·8992	·9030	·9068	·9106	·9144	38
731	·9182	·9220	·9258	·9295	·9333	·9371	·9409	·9447	·9485	·9523	
732	·9561	·9599	·9637	·9674	·9712	·9750	·9788	·9826	·9864	·9902	1 3·8
733	·9939	·9977	·0015	·0053	·0091	·0128	·0166	·0204	·0242	·0280	2 7·6
734	99°·0318	·0355	·0393	·0431	·0469	·0506	·0544	·0582	·0620	·0658	3 11·4
											4 15·2
735	99°·0695	·0733	·0771	·0808	·0846	·0884	·0922	·0959	·0997	·1035	5 19·0
736	·1073	·1110	·1148	·1186	·1223	·1261	·1299	·1336	·1374	·1412	6 22·8
737	·1449	·1487	·1525	·1562	·1600	·1638	·1675	·1713	·1751	·1788	7 26·6
738	·1826	·1863	·1901	·1939	·1976	·2014	·2051	·2089	·2127	·2164	8 30·4
739	·2202	·2239	·2277	·2315	·2352	·2390	·2427	·2465	·2502	·2540	9 34·2
740	99°·2577	·2615	·2652	·2690	·2728	·2765	·2803	·2840	·2878	·2915	37
741	·2953	·2990	·3028	·3065	·3102	·3140	·3177	·3215	·3252	·3290	
742	·3327	·3365	·3402	·3440	·3477	·3514	·3552	·3589	·3627	·3664	1 3·7
743	·3702	·3739	·3776	·3814	·3851	·3889	·3926	·3963	·4001	·4038	2 7·4
744	·4075	·4113	·4150	·4187	·4225	·4262	·4299	·4337	·4374	·4412	3 11·1
											4 14·8
745	99°·4449	·4486	·4523	·4561	·4598	·4635	·4673	·4710	·4747	·4785	5 18·5
746	·4822	·4859	·4896	·4934	·4971	·5008	·5045	·5083	·5120	·5157	6 22·2
747	·5194	·5232	·5269	·5306	·5343	·5381	·5418	·5455	·5492	·5529	7 25·9
748	·5567	·5604	·5641	·5678	·5715	·5752	·5790	·5827	·5864	·5901	8 29·6
749	·5938	·5975	·6013	·6050	·6087	·6124	·6161	·6198	·6235	·6273	9 33·3
750	99°·6310	·6347	·6384	·6421	·6458	·6495	·6532	·6569	·6606	·6643	36
751	·6681	·6718	·6755	·6792	·6829	·6866	·6903	·6940	·6977	·7014	
752	·7051	·7088	·7126	·7162	·7199	·7236	·7273	·7310	·7347	·7384	1 3·6
753	·7421	·7458	·7495	·7532	·7569	·7606	·7643	·7680	·7717	·7754	2 7·2
754	·7791	·7828	·7865	·7902	·7938	·7975	·8012	·8049	·8086	·8123	3 10·8
											4 14·4
755	99°·8160	·8197	·8234	·8271	·8308	·8344	·8381	·8418	·8455	·8492	5 18·0
756	·8529	·8566	·8603	·8639	·8676	·8713	·8750	·8787	·8824	·8860	6 21·6
757	·8897	·8934	·8971	·9008	·9044	·9081	·9118	·9155	·9192	·9228	7 25·2
758	·9265	·9302	·9339	·9376	·9412	·9449	·9486	·9523	·9559	·9596	8 28·8
759	·9633	·9670	·9706	·9743	·9780	·9816	·9853	·9890	·9927	·9964	9 32·4
760	100°·0000	·0037	·0073	·0110	·0147	·0183	·0220	·0257	·0293	·0330	36
761	·0367	·0403	·0440	·0477	·0513	·0550	·0587	·0623	·0660	·0696	
762	·0733	·0770	·0806	·0843	·0880	·0916	·0953	·0989	·1026	·1062	1 3·6
763	·1099	·1136	·1172	·1209	·1245	·1282	·1318	·1355	·1392	·1428	2 7·2
764	·1465	·1501	·1538	·1574	·1611	·1647	·1684	·1720	·1757	·1793	3 10·8
											4 14·4
765	100°·1830	·1866	·1903	·1939	·1976	·2012	·2049	·2085	·2122	·2158	5 18·0
766	·2194	·2231	·2267	·2304	·2340	·2377	·2413	·2450	·2486	·2522	6 21·6
767	·2559	·2595	·2632	·2668	·2704	·2741	·2777	·2814	·2850	·2886	7 25·2
768	·2923	·2959	·2995	·3032	·3068	·3105	·3141	·3177	·3214	·3250	8 28·8
769	·3286	·3323	·3359	·3395	·3432	·3468	·3504	·3540	·3577	·3613	9 32·4
770	100°·3649	·3686	·3722	·3758	·3794	·3831	·3867	·3903	·3940	·3976	

APPENDIX TABLE III. (continued).

Millims.	Tenths of a millimetre.										Pro.° Pts.
	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.	
770	100·3649	·3686	·3722	·3758	·3794	·3831	·3867	·3903	·3940	·3976	36
771	·4012	·4048	·4085	·4121	·4157	·4193	·4230	·4266	·4302	·4338	
772	·4374	·4411	·4447	·4483	·4519	·4555	·4592	·4628	·4664	·4700	1 3·6
773	·4736	·4773	·4809	·4845	·4881	·4917	·4953	·4989	·5026	·5062	2 7·2
774	·5098	·5134	·5170	·5206	·5242	·5278	·5315	·5351	·5387	·5423	3 10·8
											4 14·4
775	·5459	·5495	·5531	·5567	·5603	·5639	·5675	·5712	·5748	·5784	5 18·0
776	·5820	·5856	·5892	·5928	·5964	·6000	·6036	·6072	·6108	·6144	6 21·6
777	·6180	·6216	·6252	·6288	·6324	·6360	·6396	·6432	·6468	·6504	7 25·2
778	·6540	·6576	·6612	·6648	·6684	·6720	·6756	·6792	·6828	·6864	8 28·8
779	·6900	·6936	·6971	·7007	·7043	·7079	·7115	·7151	·7187	·7223	9 32·4

APPENDIX TABLE IV.—For Conversion of Water Pressure into its Equivalent in Mercury. 1 millim. Water = 0·0736 millim. Mercury.

Interpolated from table given in LANDOLT and BÖRNSTEIN'S 'Physikalisch-chemische Tabellen.'

NOTE.—Large temperature differences might influence the last figure of this table.

Water.	Mercury.	Water.	Mercury.
millims.	millims.	millims.	millims.
0·05	0·004	1·55	0·114
0·10	0·007	1·60	0·118
0·15	0·011	1·65	0·121
0·20	0·015	1·70	0·125
0·25	0·018	1·75	0·129
0·30	0·022	1·80	0·132
0·35	0·026	1·85	0·136
0·40	0·029	1·90	0·140
0·45	0·033	1·95	0·144
0·50	0·037	2·00	0·147
0·55	0·040	2·05	0·151
0·60	0·044	2·10	0·155
0·65	0·048	2·15	0·158
0·70	0·052	2·20	0·162
0·75	0·055	2·25	0·166
0·80	0·059	2·30	0·169
0·85	0·063	2·35	0·173
0·90	0·066	2·40	0·177
0·95	0·070	2·45	0·180
1·00	0·074	2·50	0·184
1·05	0·077	2·55	0·188
1·10	0·081	2·60	0·191
1·15	0·085	2·65	0·195
1·20	0·088	2·70	0·199
1·25	0·092	2·75	0·202
1·30	0·096	2·80	0·206
1·35	0·099	2·85	0·210
1·40	0·103	2·90	0·213
1·45	0·107	2·95	0·217
1·50	0·110	3·00	0·221

APPENDIX TABLE V.—Showing the value of $d \equiv T - pt$ corresponding to different values of T near 100° , deduced from the formula $d = \delta \left[\left(\frac{T}{100} \right)^2 - \frac{T}{100} \right]$.

NOTE.—Between 0° and 100° pt is greater than T , and d is negative. Above 100° pt is less than T , and d is positive.

T.	$\left(\frac{T}{100} \right)^2 - \frac{T}{100}$	$t = 1.500$.	$t = 1.510$.	$t = 1.520$.	$t = 1.530$.	$t = 1.540$.	$t = 1.550$.	$t = 1.560$.	$t = 1.570$.	$t = 1.580$.	$t = 1.590$.	$t = 1.600$.
101.0	+0.0101	+0.0151	+0.0153	+0.0154	+0.0155	+0.0156	+0.0157	+0.0158	+0.0159	+0.0160	+0.0161	+0.0162
100.9	+0.0091	+0.0136	+0.0137	+0.0138	+0.0139	+0.0140	+0.0141	+0.0142	+0.0143	+0.0144	+0.0145	+0.0146
100.8	+0.0081	+0.0121	+0.0122	+0.0123	+0.0124	+0.0125	+0.0126	+0.0126	+0.0127	+0.0128	+0.0129	+0.0130
100.7	+0.0071	+0.0106	+0.0107	+0.0108	+0.0109	+0.0109	+0.0110	+0.0111	+0.0111	+0.0112	+0.0113	+0.0114
100.6	+0.0061	+0.0091	+0.0092	+0.0093	+0.0093	+0.0094	+0.0095	+0.0095	+0.0096	+0.0096	+0.0097	+0.0098
100.5	+0.0050	+0.0075	+0.0075	+0.0076	+0.0076	+0.0077	+0.0077	+0.0078	+0.0078	+0.0079	+0.0079	+0.0080
100.4	+0.0040	+0.0060	+0.0060	+0.0061	+0.0061	+0.0062	+0.0062	+0.0062	+0.0063	+0.0063	+0.0064	+0.0064
100.3	+0.0030	+0.0045	+0.0045	+0.0046	+0.0046	+0.0046	+0.0046	+0.0047	+0.0047	+0.0047	+0.0048	+0.0048
100.2	+0.0020	+0.0030	+0.0030	+0.0030	+0.0031	+0.0031	+0.0031	+0.0031	+0.0031	+0.0032	+0.0032	+0.0032
100.1	+0.0010	+0.0015	+0.0015	+0.0015	+0.0015	+0.0015	+0.0015	+0.0016	+0.0016	+0.0016	+0.0016	+0.0016
100.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
99.9	-0.0010	-0.0015	-0.0015	-0.0015	-0.0015	-0.0015	-0.0015	-0.0016	-0.0016	-0.0016	-0.0016	-0.0016
99.8	-0.0020	-0.0030	-0.0030	-0.0030	-0.0031	-0.0031	-0.0031	-0.0031	-0.0031	-0.0032	-0.0032	-0.0032
99.7	-0.0030	-0.0045	-0.0045	-0.0046	-0.0046	-0.0046	-0.0046	-0.0047	-0.0047	-0.0047	-0.0048	-0.0048
99.6	-0.0040	-0.0060	-0.0060	-0.0061	-0.0061	-0.0062	-0.0062	-0.0062	-0.0063	-0.0063	-0.0064	-0.0064
99.5	-0.0049	-0.0073	-0.0073	-0.0074	-0.0075	-0.0075	-0.0076	-0.0076	-0.0077	-0.0077	-0.0078	-0.0078
99.4	-0.0059	-0.0088	-0.0089	-0.0090	-0.0090	-0.0091	-0.0091	-0.0092	-0.0093	-0.0093	-0.0094	-0.0094
99.3	-0.0069	-0.0103	-0.0104	-0.0105	-0.0106	-0.0106	-0.0107	-0.0108	-0.0108	-0.0109	-0.0110	-0.0110
99.2	-0.0079	-0.0118	-0.0119	-0.0120	-0.0121	-0.0122	-0.0122	-0.0123	-0.0124	-0.0125	-0.0126	-0.0126
99.1	-0.0089	-0.0133	-0.0134	-0.0135	-0.0136	-0.0137	-0.0138	-0.0139	-0.0140	-0.0141	-0.0142	-0.0142
99.0	-0.0099	-0.0148	-0.0149	-0.0150	-0.0151	-0.0152	-0.0153	-0.0154	-0.0155	-0.0156	-0.0157	-0.0158
98.9	-0.0109	-0.0163	-0.0164	-0.0166	-0.0167	-0.0168	-0.0169	-0.0170	-0.0171	-0.0172	-0.0173	-0.0174
98.8	-0.0118	-0.0177	-0.0178	-0.0179	-0.0181	-0.0182	-0.0183	-0.0184	-0.0185	-0.0186	-0.0188	-0.0189
98.7	-0.0128	-0.0192	-0.0193	-0.0195	-0.0196	-0.0197	-0.0198	-0.0200	-0.0201	-0.0202	-0.0204	-0.0205
98.6	-0.0138	-0.0207	-0.0208	-0.0210	-0.0211	-0.0213	-0.0214	-0.0215	-0.0217	-0.0218	-0.0219	-0.0221
98.5	-0.0147	-0.0220	-0.0222	-0.0223	-0.0225	-0.0226	-0.0228	-0.0229	-0.0231	-0.0232	-0.0234	-0.0235
98.4	-0.0157	-0.0235	-0.0237	-0.0239	-0.0240	-0.0242	-0.0243	-0.0245	-0.0246	-0.0248	-0.0250	-0.0251
98.3	-0.0167	-0.0250	-0.0252	-0.0254	-0.0256	-0.0257	-0.0259	-0.0261	-0.0262	-0.0264	-0.0266	-0.0267
98.2	-0.0177	-0.0265	-0.0267	-0.0269	-0.0271	-0.0273	-0.0274	-0.0276	-0.0278	-0.0280	-0.0281	-0.0283
98.1	-0.0186	-0.0279	-0.0281	-0.0283	-0.0285	-0.0286	-0.0288	-0.0290	-0.0292	-0.0294	-0.0296	-0.0298
98.0	-0.0196	-0.0294	-0.0296	-0.0298	-0.0300	-0.0302	-0.0304	-0.0306	-0.0308	-0.0310	-0.0312	-0.0314

APPENDIX II. [Added December 1, 1899.]

We think we are justified in adding, in the form of an appendix, some further considerations on the question of the sulphur boiling-point, the results of which we obtained since the date of handing in the paper. On p. 99 of the text are given the observations of REGNAULT on the variation of the boiling-point of sulphur with pressure near 760 millims. The formula used by REGNAULT himself to express the results of his observations over the whole range was of a logarithmic kind, and gave for the pressure 760 millims. the value $448^{\circ}38$. If, however, we disregard the extreme portions of the range and find a formula to represent only those observations near the normal pressure, we find for this point a value nearly a degree lower.

Taking the four observations quoted in the text, and representing them by a formula

$$T = a + bp + cp^2,$$

of which the constants a , b , and c are determined by least squares, we find for $p = 760$ the value $447^{\circ}51$, with residuals very much smaller than those given by the logarithmic formula. We are aware that to represent four observations by a formula with three constants is not giving very much latitude for probable errors, but we think, nevertheless, that $447^{\circ}5$ gives much more nearly the true result to be deduced from REGNAULT'S experiments than his own much higher figure. Accepting this method of treating his observations, we further find that instead of the value for dt/dp $0^{\circ}082$ per millim. as given by the logarithmic formula, we get $0^{\circ}088$, a value very appreciably higher.

If our determinations of pt , had all been made at 760 millims. pressure, or if this had been the mean pressure of each different series, the value to be taken for dt/dp would have been of no great consequence, but as in each case the mean pressure fell appreciably below this, we thought it desirable to see how much the assumption of the higher value might influence the results of our experiments.

We gave in the text the results of some calculations on the series of sulphur points taken with the Kew platinum thermometers K.1 and K.3, made with the object of arriving at an independent value for dt/dp . Dr. CHREE has recently completed for publication an investigation into the behaviour of the Kew platinum thermometers, and their permanence over a considerable period, and finds that, when one or two sources of uncertainty are eliminated, the values we gave for dt/dp for K.1 and K.3 are both somewhat too small. He has courteously permitted us to state that the most probable value for this number deducible from the different series of determinations of the sulphur point, which he has worked up, is much more nearly

0°·090 than 0°·082, agreeing in a remarkable manner with the result we have just deduced from REGNAULT'S experiments.

As the mean pressure of our sulphur point determinations was below 760 millims. in all the series, we thought it of interest to recalculate the results of each set, applying the value 0·088 for dt/dp . Combining this with the known value of $d.pt/dt$, we have for $d.pt/dp$ the value 0·0773 at 445°.

The values of pt , from the separate experiments with K.8 and K.9, are given in the following table :—

K.8.	K.9.
421·58	421·46
·56	·42
·52	·49
·53	·49
·56	·44
·57	
·59	
<hr/> 421·559	<hr/> 421·460

These values of pt , only differ very slightly from those previously found.

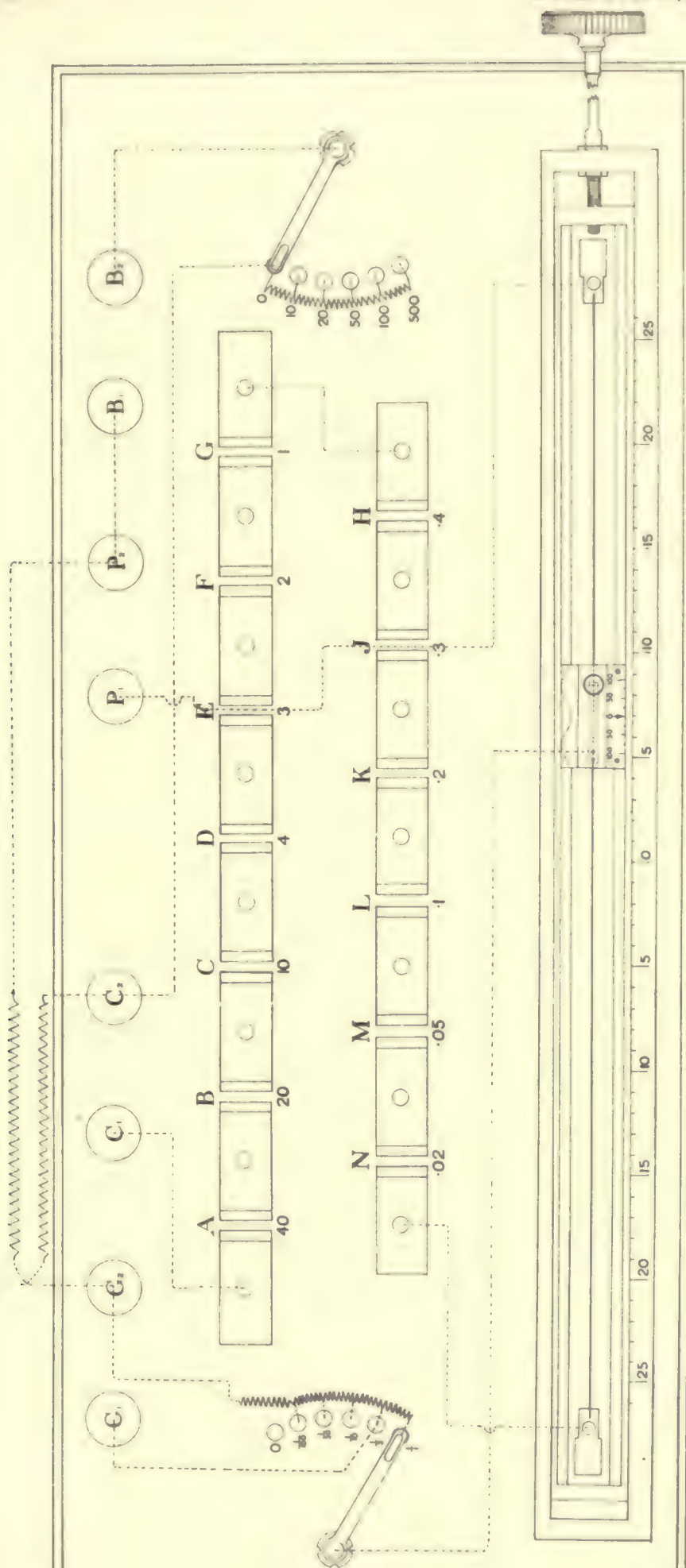
We next proceed to find for each thermometer from the equivalent values of T and pt given by the comparisons near the sulphur point the T , corresponding to the value of pt , deduced above. We formerly used for this purpose a formula containing the term $(pt - pt_0)$ to the first and second powers, but as there appeared some doubt as to how the result might be affected by stopping short at the second term, in the new calculation we tried several formulæ of different types, and included varying numbers of experiments in the neighbourhood of the sulphur point.

We had already satisfied ourselves that CALLENDAR'S formula closely represents the divergence between the platinum and gas scales over the range covered by our experiments. Utilising this formula and including for K.8 all the experiments between $T = 412^{\circ}\cdot65$ and $T = 455^{\circ}\cdot54$, nine in all, we obtain for the T , corresponding to the pt , above given the value $445^{\circ}\cdot27$, which is sensibly identical with that previously found. For the two series with K.9, however, we find that while the first series of observations gives a result for T , $445^{\circ}\cdot27$, the second series, including the comparisons between $T = 405^{\circ}\cdot93$ and $T = 450^{\circ}\cdot58$, gives $445^{\circ}\cdot05$, which is appreciably lower than the result given in the text. The discrepancy between the two values furnished by the thermometer K.9 is lessened by excluding some of the comparisons which are at some distance from the sulphur point, but the mean result is hardly sensibly affected.

We have also made the same kind of calculation of a value for T , from the comparisons with thermometer K.2, though, in this case, none of the comparisons were made at temperatures very near the sulphur point. We find, employing the same

formula to obtain the T_s , the value $445^{\circ}\cdot 1$, which is only $0^{\circ}\cdot 1$ lower than the mean previously found from the K.8 and K.9 experiments. During this series of comparisons the pressure of the nitrogen in the gas thermometer was sensibly lower than in any of the preceding ones, being only 392 millims. instead of 529 millims.

In view of the uncertainties in the value of dt/dp and those arising from imperfect data as to the expansion of the porcelain at high temperatures, we prefer to suppress the hundredths of a degree from our mean result for the temperature of the boiling-point of sulphur, and to give for this point the value $T_s = 445^{\circ}\cdot 2$ *on the scale of the constant volume nitrogen thermometer.*



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III. *On the Propagation of Earthquake Motion to Great Distances.*

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Communicated by Sir ROBERT S. BALL, F.R.S.

Received June 16,—Read November 16, 1899.

§ 1. THE earliest suggestion of the existence of more than one kind of wave motion in an earthquake appears to have been made in 1849 by Wertheim.* After discussing on theoretical grounds the ratio between the rates of propagation of distortional and condensational waves in an infinite solid, he proceeds to say that the only possible experimental verification would be by the use of a very large body, such as the Earth itself. It would hardly be possible to produce, artificially, a disturbance which would be propagated and be sensible at a great distance from the origin, but such disturbances are produced naturally in earthquakes, and he finds in the descriptions of great earthquakes indications of two distinct types of disturbance, which succeed each other in point of time, and which he attributes to the two forms of elastic wave motion.

Suggestive as it is, this memoir seems for long to have been devoid of influence on seismological research. It would not be materially incorrect to say that ROBERT MALLETT'S classic works were based on the hypothesis that earthquake motion was solely that of a condensational wave.

In 1885, Lord RAYLEIGH published his investigation† of elastic surface waves, that is to say, superficial waves analogous to deep-water waves, but owing their propagation to the elasticity of the substance in which they are propagated instead of to gravity. The concluding passage of this paper suggests that "it is not improbable that the surface waves here investigated play an important part in earthquakes, and in the collision of elastic solids. Diverging in two dimensions only, they must acquire at a great distance from the source a continually increasing preponderance."

In the year 1888, a paper‡ by Professor C. G. KNOTT was published, in which he

* G. WERTHEIM, "Mémoire sur la Propagation du Mouvement dans les Corps solides et liquides" 'Comptes Rendus,' vol. 29, 1849, pp. 697-700; 'Ann. Chim. Phys.,' 3rd ser., vol. 21, 1851, pp. 19-36).

† "On Waves propagated along the Plane Surface of an Elastic Solid" ('Proc. Lond. Math. Soc.,' vol. 17, 1885, pp. 4-11).

‡ "Earthquakes and Earthquake Sounds as Illustrations of the General Theory of Elastic Vibrations" ('Trans. Seismol. Soc. Japan,' vol. 12, 1888, pp. 115-136).

shows that no separation of the condensational and distortional waves is to be expected in the records of seismographs. Wave motion of either kind, on passage from one medium to another, is split up into refracted and reflected waves, while each of these is again split up into condensational and distortional waves. The result of this is that, even if earthquake motion were purely condensational or distortional at first, it would soon become converted, in its passage through the heterogeneous materials of the earth's crust, into an extremely complex disturbance, analogous to that registered by seismographs.

He also refers to Lord RAYLEIGH's paper, but considers that the comparatively large vertical and small horizontal displacements required by the theory are not in accordance with the records of seismographs. Professor MILNE has, however, lately suggested* that the records of the seismographs may be misleading, and the large horizontal displacements registered by them be due to tilting of the instruments, and not to the inertia of the supposed steady points.

Another suggestion in the paper is that the principal disturbance in an earthquake is not purely elastic, but quasi-elastic, and that what are known as the preliminary tremors are truly elastic vibrations, set up by and outracing these.

The same volume of 'Transactions' contains a paper by Professor MILNE,† in which he suggests that the effect of compressional waves propagated direct from the origin to the surface is confined to the neighbourhood of the epicentre, and that beyond this the earthquake motion felt and recorded is due to surface waves, set up at the outcrop of the waves of compression near the origin, and thence propagated outwards.

In 1894, Wertheim's memoir appears for the first time to have influenced seismological research, when it was recalled to notice by Dr. A. CANCELLI,‡ who considered that in the records of earthquakes near, and at a distance from, their origin, he could trace the separation of the condensational and distortional waves, having rates of propagation of about 5 and 2·5 kiloms. per second respectively. In his earlier paper he considered that it was only the latter which preserved sufficient energy to make them recognisable, by instrumental aid, at a distance from the origin, while the condensational waves were only recognisable in its vicinity. It is clear, however, from his paper, and from two others subsequently written§ in defence of the ideas promulgated in it, that the disturbance which he attributes to the distortional waves is the phase of great surface undulations, travelling like the waves of the sea, which

* 'Seismology,' 8vo., London, 1898, p. 117.

† J. MILNE, "On certain Seismic Problems demanding Solution" ('Trans. Seismol. Soc. Japan,' vol. 12, 1888, pp. 107-113).

‡ "Sulle ondulazioni provenienti dei centri sismici lontani" ('Ann. Ufficio Cent. Met. e Geodyn. Italiano,' 2nd series, vol. 15, 1894, Part 1, pp. 13-24).

§ "Intorno ad alcune obiezioni relative alla velocità di propagazione delle onde sismiche" ('Atti, R. Acc. Lincei,' vol. 3, 1894, Part 2, pp. 30-32); "Osservazioni e risultati recenti sulla forma e sul modo di propagarsi delle ondulazioni sismiche" ('Bol. Soc. Sismol. Ital.,' vol. 2, 1896, Part I, pp. 125-137).

do not appear to be due to distortional waves of the character contemplated by the theory of wave motion in an infinite solid, but rather to be analogous to the elastic surface waves investigated by Lord RAYLEIGH.

The views of Dr. CANCANI have been opposed by Dr. AGAMENNONE, who, in a series of papers devoted to the investigation of the observed rate of propagation of earthquakes, has shown that there is no indication of the velocities grouping themselves round the values 5 and 2·5 kiloms. per second deduced by Dr. CANCANI, but that, on the other hand, the observed values exhibit a great diversity, and not infrequently rise to double of the greater of the two assumed values.

Dr. CANCANI's views have, however, been accepted by other seismologists, notably by Professor GRABLOWITZ, who has, without any marked success, attempted to apply them to the determination of the place of origin of distant earthquakes observed at Ischia. The idea that the surface undulations due to great earthquakes are of the nature of distortional, and the so-called "preliminary tremors" of condensational, waves, seems to have taken root, and in the two most recent papers dealing with the subject by Professor C. G. KNOTT* and Professor J. MILNE,† the former are distinctly treated as distortional waves travelling by a brachistochronic path through the earth.

When investigating the great Indian earthquake of 1897, I found that the numerous diagrams, for which I was indebted to the generosity of the Directors of the Italian Observatories, showed two distinct phases, or periods of disturbance, preceding the advent of the surface undulations of long period. The first of these was marked by the commencement of the disturbance, the second by a sudden increase, accompanied by a change in the period of the waves; these features were more or less distinctly exhibited by all the records, and when preparing my report I suggested‡ that they represented the arrival of the condensational and distortional waves respectively, which had travelled through the earth, while the surface undulations of long period had travelled round the surface of the earth; thus recognising the presence of the three known types of elastic wave motion.

In this report the suggestion had to remain as such. To have entered on an examination of the records of other earthquakes with a view to its confirmation would have been foreign to the task in hand, besides being rendered impossible by the necessity of completing the report, and it is the object of this paper to show that the records of other great earthquakes confirm the suggestion.

§ 2. The rate of propagation of earthquake waves is a subject which has for long attracted much attention and been the subject of many studies and experiments. I found, however, that none of these with which I have become acquainted could be directly used, and that it was necessary to go back to the original descriptions, and

* "The New Seismology" ('Scottish Geog. Mag.,' vol. 15, 1899, pp. 1-12).

† "Earthquake Precursors" ('Nature,' vol. 59, 1899, pp. 414-416).

‡ "Mem. Geol. Surv. Ind.," vol. 29, 1899.

treat the matter anew. With the exception of some studies of the rate of propagation of earthquakes within the seismic area, the published calculations deal, almost without exception, with isolated observations, not infrequently with earthquakes whose place or time of origin are more or less uncertain, and seldom take any notice of more than the time of commencement of the record, and in some cases also of the maximum displacement.

The very laborious series of researches by Dr. AGAMENNONE I have been unable to make use of, owing to the method of calculation adopted by him. The time, accurately determined at some place away from the origin, is taken, and the distances from the origin of that place, and of the more distant places whence observations have been obtained, are calculated; thence the apparent surface velocity is obtained by dividing the difference of distance by the difference of time. This method would be perfectly legitimate if we were dealing with only one class of wave motion, propagated at a uniform rate round the surface of the earth; if, on the other hand, the wave motion is propagated along a brachistochronic path through the earth, it must necessarily lead to misleading results, owing to the difference between the true and apparent rates of propagation, a difference which varies with the distance from the origin.

The object of this study being to determine whether the three phases recognised in the records of the great earthquake of 1897 are a constant or an accidental feature, as well as to ascertain the forms of wave motion and wave-path represented by each phase, it is essential that the time intervals should be referred to the time of origin, and not of arrival of the shock at some place away from it. It is also necessary that these time intervals, as well as the distances from the place of origin, should be determined with a close degree of accuracy, as without this it would be impossible to decide whether an apparent resemblance in the records of different earthquakes was, or was not, due to the same cause in each case.

To ensure this accuracy, it is necessary to select the earthquakes dealt with. In the *first* place, it is essential that the disturbance should originate in a single effort of short duration. Fortunately all those which fulfil the other conditions fulfil this also, and none have had to be rejected on this score. *Secondly*, the time and place of origin must be tolerably accurately known. The limits of error adopted have been 1 minute of time and 1° of arc. In the case of all the earthquakes noticed below, these limits are not exceeded, and in several cases the limit of error from this cause is much less. *Thirdly*, I have excluded all cases where there were not a sufficient number of independent records to serve as a check on, and confirmation of, each other. *Fourthly*, as a separation of the condensational and distortional plane waves is not to be looked for in the heterogeneous materials near the surface of the earth, the records from places at distances of less than 20° of arc from the origin have not been taken into consideration.

In collecting the facts I have been almost exclusively indebted to the careful

and detailed accounts of earthquakes, both sensible and insensible, recorded in Italy, which are regularly published through the enlightened liberality of the Italian Government. Detailed descriptions of the records of most of the more important seismographs established in Italy have been printed, at first in the *Bollettino* of the Central Meteorological Office in Rome, and afterwards in that of the Italian Seismological Society. From these I have extracted the times of (1) the commencement of the record, (2) of any marked sudden increase of movement, and (3) of any change in its character, so far as these are mentioned; the results, in the case of the seven earthquakes which satisfy the conditions laid down, are given below.

Details of the Data.

1. JAPAN, March 22, 1894.

This earthquake has been made the subject of a special study by the late E. VON REBEUR PASCHWITZ,* by whom the three-phase character of the record was recognised. The origin is placed by Professor MILNE as in about N. lat. 43° , E. long. 146° . The time was recorded at Tokio, by the Gray-Milne seismograph, at $10^{\text{h}} 27.8^{\text{m}}$,† and the distance from the epicentre being about 950 kiloms., the time at the epicentre, reckoning the rate of propagation as 3 kiloms. per second, would be $10^{\text{h}} 22.5^{\text{m}}$. As the records are detailed in the paper referred to, it will be unnecessary to reproduce the descriptions, and they may be tabulated at once, the times being minutes after 10^{h} .

Locality.	1st phase.	2nd phase.	3rd phase.	
			Commencement.	Maximum.
Charkow . .	34.5	—	—	—
	35.7	—	—	—
Nicolaiew . .	35.2	—	62.0	—
Pavia	—	—	—	78.0
Siena	37.2	47.8	67.4	—
Rome	37.3	47.0	68.0	80.0
	37.8	—	—	—
Rocca di Papa .	37.0	48.0	68.0	79.5
	37.3	48.0	—	—

The times at Padua (40^{m}) Grenoble (39.7^{m}) and Mineo (42.5^{m}) appear to represent the maximum of the first phase, registered at Rome about 40^{m} , rather than the commencement. Besides this the Charkow and Nicolaiew pendula registered an earlier shock, presumably from the same centre, with an origin at $5^{\text{h}} 24^{\text{m}}$. The times in minutes after 5^{h} are

* 'Petermann's Mittheilungen,' 1895, pp. 14-21.

† All times are Greenwich Mean Time.

Locality.	1st phase.	2nd phase.	3rd phase.	
			Commencement.	Maximum.
Charkow . . .	—	48·6	—	—
	—	49·8	60·0	—
Nicolaiew . .	(41·0)	48·0	64·8	70·0

The time of commencement of the record at Nicolaiew is obviously late, and corresponds rather to the maximum than the commencement of the first phase.

Converting these times into intervals, and distinguishing the earlier shock as (1), the principal one as (2), we get

Arc degrees.	Locality.	1st phase.	2nd phase.	3rd phase.	
				Commencement.	Maximum.
68·7	Charkow . . (1) . .	—	24·6	—	—
		—	25·8	36·0	—
	(2) . .	12·0	—	—	—
72·9	Nicolaiew . . (1) . .	13·2	—	—	—
		—	24·0	40·8	46·0
	(2) . .	12·7	—	39·5	—
83·9	Pavia . . . (2) . .	—	—	—	55·5
84·6	Siena . . . (2) . .	14·7	25·3	44·9	—
85·4	Rome . . . (2) . .	14·8	24·5	45·5	57·5
		15·3	—	—	—
85·4	Rocca di Papa (2) . .	14·5	25·5	45·5	57·0
		14·8	25·5	—	—

2. ARGENTINE, October 27, 1894.

According to an account of this earthquake by A. F. NOGUÈS,* the zone of greatest intensity formed an ellipse whose major axis passed by Rioja, San Juan, and Mendoza, while the minor axis reached nearly to the foot of the Andes. The epicentre may be safely placed in S. lat. $28^{\circ} 30'$, W. long. $69^{\circ} 0'$, with an error of less than 1° of arc.

The time of origin is not so easy to determine. It was recorded in the observatory of Santiago de Chile at $4^{\text{h}} 7^{\text{m}} 40^{\text{s}}$ P.M. local mean time. I have not been able to obtain the exact meridian of this observatory, but it is, according to the best atlases, about 2^{m} east of Valparaiso, whose local time is $4^{\text{h}} 46^{\text{m}} 5^{\text{s}}$ slow of Greenwich. Applying this correction the G.M.T. (civil) at Santiago becomes about $20^{\text{h}} 52^{\text{m}}$. The only other time observation of any value is that from Buenos Ayres, where it was recorded at $5^{\text{h}} 2^{\text{m}}$ local time, which is about $3^{\text{h}} 53^{\text{m}} 5^{\text{s}}$ slow of Greenwich; the time at

* 'Comptes Rendus,' vol. 120, 1895, pp. 167-170.

which the earthquake was experienced corresponded therefore to about 20^h 55.5^m Greenwich time.

Allowing for a rate of propagation of 3 kiloms. per second, the earthquake would have taken about 2^m to reach Santiago, and 6^m to reach Buenos Ayres. Making these deductions, the time of origin becomes 20^h 50^m and 20^h 49.5^m respectively. As greater value should be attached to the Santiago record, both because it was automatic and because of its greater proximity to the centre, we may take the time of origin as 20^h 50^m \pm 0.5^m.

The records abstracted below, except in the case of Tokio, are taken from the 'Bollettino d. Ufficio Centrale Met. e Geodyn.,' for October, 1894.

Pavia.—21^h 46^m 55^s commencement, 21^h 57^m 52^s end, on the Brassart seismograph.

Siena.—21^h 12^m commencement on the Vicentini microseismograph, slow undulations distinct at 21^h 52^m, which continue conspicuous till 22^h 8^m.

Rome.—21^h 7^m 35^s commencement on both components of the grande sismom. On the N.W.—S.E. component these reach a maximum of 3.5 millims. at 21^h 15^m 10^s; towards 21^h 40^m slow undulations begin on both components. Maximum at 21^h 55^m 40^s, end about 23^h. On the other seismograph the commencement is not till 21^h 40^m, maximum 21^h 55^m 40^s, end 22^h 14^m 15^s.

Ischia.—21^h 33^m commencement on the Brassart seismograph; 22^h 8^m maximum, end at 22^h 40^m.

Rocca di Papa.—21^h 49^m 35^s commencement, 22^h 10^m end, on the grande sismom.

Nicolaiew.—Commencement 21^h 12^m 6^s, a sudden increase at 22^h 17^m 6^s, curve disappears from 21^h 24^m 6^s to 21^h 32^m 6^s, fresh disappearance till 22^h 2^m 6^s, end 0^h 37^m 6^s of following day.

Charkow.—Commencement 21^h 8^m 36^s, the curve disappeared for an hour, end at 0^h 10^m 54^s of the following day.

Tokio.—In a letter by Dr. E. VON REBEUR PASCHWITZ to 'Nature' (vol. 52, p. 55, 1895), a letter from Professor MILNE is referred to, in which it is stated that the earthquake was recorded at Tokio by three instruments at 18^h 0^m, 18^h 5^m, 17^h 41^m, respectively. The times were measured from a time signal at about the previous noon, but the record of these was lost by fire. In the case of the first instrument the time signal was always impressed within about $\frac{1}{2}$ ^m or 1^m of noon, consequently the error cannot exceed a few minutes. These times, recorded also in 'Brit. Assoc. Rep.,' 1895, p. 147, where the last is marked as evidently wrong, correspond to Greenwich mean times 21^h 0^m, 21^h 5^m, and 20^h 41^m respectively.

The times, given in minutes after 21^h Greenwich mean time, may be classified as follows :—

Locality.	1st phase.	2nd phase.	3rd phase.	
			Commencement.	Maximum.
Pavia	—	—	46·9	—
Siena	(12·0)	—	—	52·0
Rome	7·6	15·2	40·0	55·7
	—	—	40·0	55·7
Ischia	—	—	(33·0)	68·0
Rocca di Papa . .	—	—	49·6	—
Nicolaiew	(12·1)	17·1	—	—
Charkow	8·6	—	—	—
Tokio	(0·0)	—	—	—
	(5·0)	—	—	—

The times of commencement at Siena and Nicolaiew evidently correspond to the maximum rather than the commencement of the first phase as recorded at Rome. The sudden increase in the disturbance at Nicolaiew at 17·1^m is attributed to the second phase. It is in tolerably, though not close, concordance with the time at Rome.

The times of commencement at Tokio are, in spite of the much greater distance from the origin, much earlier than the corresponding times at the European observatories, and the difference seems greater than can be attributed to instrumental errors. The commencement of the third phase at Ischia is so much in advance of the others that it is probably not strictly comparable with them, and refers to a somewhat different phase.

Converted into intervals these times become

Arc degrees.	Locality.	1st phase.	2nd phase.	3rd phase.	
				Commencement.	Maximum.
102·2	Pavia	—	—	56·9	—
102·7	Siena	—	—	—	62·0
102·8	Rome	17·8	25·2	50·0	65·7
		—	—	50·0	65·7
102·9	Rocca di Papa . .	—	—	59·6	—
103·0	Ischia	—	—	—	78·0
117·6	Nicolaiew	—	27·1	—	—
120·9	Charkow	18·6	—	—	—

3. JAPAN, June 15, 1895.

This earthquake has been discussed by Professor MILNE,* who puts the time and

* 'Brit. Assoc. Rep.,' 1897, p. 157.

place of origin as 10^h 31^m on 15th June, at about 120 geographical miles east of Migako, or in about N. lat. 39° 30', E. long. 144° 30'.

The following abstract of the records is taken from 'Boll. Soc. Sismol. Ital.,' vol. 2, Part II.

Padua.—Commencement of rapid vibrations at 10^h 46^m 57^s, which terminate at 11^h 4^m 27^s; at 11^h 17^m 17^s the first groups of slow undulations, period 40^s, commences; record ends at 12^h 58^m 1^s.

Rocca di Papa.—10^h 56^m 18^s commencement of barely perceptible tremors on the N.—S. component of the grande sismom; at 11^h 20^m commencement of undulations of 18^s period, which reach a maximum of 11^h 23^m 15^s, and end at about 12^h 30^m. On the E.—W. component the tremors begin at 10^h 57^m, and the long waves at 11^h 17^m 48^s, maximum at 11^h 23^m 10^s, and end at 12^h 30^m.

Rome.—On the sismom. medio undulations began at 11^h 19^m 20^s and end about 11^h 32^m 30^s. The grande sismom. shows a commencement at 11^h 21^m 50^s, maximum 11^h 28^m 25^s, end 11^h 47^m 15^s, all on the N.E.—S.W. component. The other component shows a commencement at 11^h 19^m 55^s, maximum at 11^h 23^m 5^s, end at 11^h 49^m 20^s.

Ischia.—10^h 50^m 29^s, commencement of record on horizontal pendula (according to 'Brit. Assoc. Report,' 1897, p. 170, the time was 10^h 49^m 50^s) at 10^h 57^m 21^s the movement, which had been minute, became appreciable; at 11^h 6^m 10^s the period of the undulations increased, and the great undulations commenced at 11^h 22^m, end at 12^h 30^m.

Catania.—The account is very meagre, but in the 'Atti. Acc. Gioenia di Sci. Nat.,' ser. 4, vol. 10, the following details of the record are given. Commencement 10^h 47^m 12^s; commencement of waves of about 24^s period 11^h 9^m, maximum 11^h 29^m 15^s, end 14^h 2^m.

At *Shide* the horizontal pendulum is reported to have commenced its record at 10^h 30^m, and at Nicolaiew the maximum was at 10^h ('Brit. Assoc. Report,' 1897, pp. 149, 167), these times being in advance of the time of origin of the shock.

Classifying these, we get the following times in minutes after 10^h A.M.

	1st phase.	2nd phase.	3rd phase.	
			Commencement.	Maximum.
Padua	47·0	—	77·3	—
Rocca di Papa .	—	56·3	80·0	83·0
Rome "	—	57·0	77·8	83·2
" "	—	—	79·3	—
" "	—	—	81·8	88·4
" "	—	—	79·9	83·1
Ischia	(49·8)	57·3	(66·2)	88·0
Catania	47·2	—	(69·0)	89·2

The time of commencement of the first phase at Ischia, 10^h 49·8^m, is evidently late

and corresponds to the maximum rather than the commencement of the same phase at Padua and Catania, while the recorded times of commencement of the slow undulations at Ischia and Catania are so much in advance of these at the other stations that they must be regarded as due to an earlier phase, while the undulations were still too small to be generally registered.

There were two other shocks registered on the same day in Japan, and presumably originating from the same, or practically the same, centre. Making the same time allowance the times of origin would be $19^h 13.25^m$ and $22^h 58^m$ of 15th June. From the records published in the 'Boll. Soc. Sismol. Ital.,' vol. 2, Part II., the following details are extracted.

Shock of $19^h 13.2^m$.

Padua.— $19^h 28^m 41^s$ commencement of rapid oscillations, at $20^h 3^m 33^s$ the slow undulations commence, which end at $20^h 22^m 43^s$.

Rocca di Papa.—Commencement $20^h 3^m$, maximum $20^h 6^m$, end $20^h 24^m$ on N.—S. component; on E.—W. commencement $20^h 4^m$, maximum $20^h 6^m$, end $20^h 17^m$.

Rome.—The first distinct oscillations at $20^h 4^m 15^s$ on N.W.—S.E. component, maximum $20^h 6^m 55^s$, end $20^h 22^m 30^s$. On the other component the commencement was at $20^h 8^m 55^s$, end $20^h 25^m 10^s$.

Ischia.— $19^h 38^m 47^s$ commencement on both the horizontal pendula; oscillations of a period of 22.6^s commenced at $20^h 3^m 7^s$ on E.—W. component and at $20^h 3^m 33^s$ on N.—S.; maximum at $20^h 6^m 47^s$.

Summary of the above Times, in minutes, after 19^h .

Locality.	1st phase.	2nd phase.	3rd phase.	
			Commencement.	Minimum.
Padua. . . .	28.7	—	63.5	—
Rocca di Papa .	—	—	63.0	66.0
	—	—	64.0	66.0
Rome	—	—	64.2	66.9
	—	—	68.9	—
Ischia	—	38.8	63.1	66.8
	—	38.8	63.5	—

Shock of $22^h 58^m$.

Padua.— $23^h 13^m 27^s$ commencement of diagram, at $23^h 13^m 46^s$ the slow undulations began, which terminated at $24^h 0^m 24^s$.

Rocca di Papa.— $23^h 46^m$ commencement on N.—S. component, $23^h 49^m$ maximum, end 24^h . On E.—W. component the commencement was $23^h 48^m$, maximum, $23^h 50^m 30^s$, end about 24^h .

Ischia.—Commencement of disturbance on E.—W. component $23^h 23^m 23^s$; the slow

undulations commenced at 23^h 49^m 15^s, and at 23^h 49^m 31^s on the N.—S. The terminations of the diagrams were at 24^h 13^m 27^s and 24^h 17^m 7^s respectively.

Summary of the above Times, in minutes, after 23^h.

Locality.	1st phase.	2nd phase.	3rd phase.	
			Commencement.	Maximum.
Padua	13.5	—	49.8	—
Rocca di Papa .	—	—	46.0	49.0
	—	—	48.0	50.5
Ischia	—	23.4	49.2	—
	—	—	49.5	—

Combining these three groups of records, and distinguishing the shocks as (1), (2), (3), respectively, we get the following time intervals:—

Arc degrees.	Locality.	1st phase.	2nd phase.	3rd phase.	
				Commencement.	Maximum.
85.1	Padua . . . (1) . .	16.0	—	46.3	—
		(2)	—	50.3	—
		(3)	—	57.8	—
87.7	Rocca di Papa (1) . .	—	25.3	49.0	52.0
		—	26.0	46.8	52.2
		—	—	49.8	52.8
		—	—	50.8	52.8
		—	—	48.0	57.0
87.7	Rome . . . (1) . .	—	—	50.0	52.5
		—	—	48.3	—
		—	—	50.8	57.4
		—	—	48.9	52.1
		—	—	51.0	53.7
88.0	Ischia . . . (1) . .	—	—	55.7	—
		—	26.3	—	57.0
		—	25.6	49.9	53.6
		—	25.6	50.3	—
90.9	Catania . . (1) . .	—	25.4	51.2	—
		16.2	—	51.5	—
		—	—	—	58.2

4. JAPAN, August 31, 1896.

According to Professor MILNE,* this earthquake had its epicentre in about N. lat. 39° 40', E. long. 140° 50'. The time of origin was 5^h 7^m 9^s P.M. Japan time or 8^h 7^m 9^s Greenwich time. These data may be accepted as correct, so far as the

* 'Brit. Assoc. Rep.' 1897, p. 162.

geographical position of the epicentre is concerned, and the time error is probably under 0.25^m . The time may, therefore, be taken as $8^h 7^m$. The abstract of the records in Europe is taken from the 'Boll. Soc. Sismol. Ital.,' vol. 2, Part II., except in the case of the records from the Isle of Wight, which are abstracted from 'Brit. Assoc. Report,' 1896, p. 229.

Nicolaiew.— $8^h 7.5^m$ commencement, $8^h 17^m$ sudden increase; $8^h 30^m$, width of trace 10 millim., $8^h 33^m$ disappearance of ditto, end at $11^h 7^m$.

Strassburg.—Commencement $8^h 17^m 50^s$, maximum $8^h 29^m 56^s$, end $11^h 38^m 2^s$ ('Nature,' vol. 55, p. 558).

Isle of Wight.—Commencement at Carisbrooke Castle $8^h 23^m 6^s$, exceedingly minute tremors; first decided tremors $8^h 31^m 46^s$ at Carisbrooke, $8^h 31^m 42^s$ at Shide; heavy motion commences $8^h 57^m 6^s$ and $56^m 49^s$ respectively, maximum, first at $9^h 4^m 26^s$, and absolute at $14^m 26^s$, both at Carisbrooke; end of disturbance $11^h 16^m 20^s$, and $10^h 59^m 36^s$.

Rocca di Papa.—Horizontal pendula; commencement $8^h 31^m$; these undulations had a period of 30^s and at 9^h the character of the record changed to undulations of 14^s , attaining their maximum at $9^h 4^m$; end of disturbance about 10^h .

Seismograph of 7^m . Commencement $8^h 55^m$, maximum $9^h 4^m$, end $9^h 6.5^m$.

Seismograph of 15^m . E.—W. component: commencement $8^h 21^m$, disturbance becomes very distinct at $8^h 32^m 30^s$; $8^h 41^m$ commencement of waves of 30^s period, which change to 14^s period at $8^h 59^m 30^s$, maximum of these $9^h 4^m$, end at $10^h 16^m$; N.—S. component: first visible tremors $8^h 21^m$, which became distinct at $8^h 31.5^m$; $8^h 40^m$ commencement of waves of 30^s period, which change to 14^s period at $8^h 58^m 30^s$, maximum $9^h 4^m$, end $10^h 0^m$.

Rome.—Sismom. grande, 16^m , 200 kilogs., N.E.—S.W. component: $8^h 21^m 15^s$ commencement, after a diminution a group of oscillations recommences at $8^h 31^m 10^s$, at $8^h 58^m 20^s$ the slow undulations commence, maximum, $9^h 4^m 15^s$, end $9^h 24^m 35^s$; N.W.—S.E. component: commencement not distinctly determinable, but becomes distinct at $8^h 24^m$. Somewhat considerable oscillations commence at $8^h 29^m 55^s$, with a maximum at $8^h 32^m 20^s$; the slow undulations commence at $8^h 58^m 40^s$, maximum $9^h 3^m 55^s$, end $9^h 25^m 50^s$.

Ischia.—Horizontal pendula; commencement of first phase $8^h 20^m 30^s$, of second phase $8^h 31^m 30^s$, of third phase of long undulations $8^h 49^m 41^s$, maximum $9^h 6^m$, end $10^h 21^m$.

Catania.—Commencement $8^h 25^m 24^s$; at $9^h 32^m 24^s$ commencement of another group of oscillations of greater amplitude; maximum of slow undulations about $9^h 4^m$; N.W.—S.E. component gives a much better record, commencement $8^h 21^m 48^s$; at $8^h 32^m 33^s$ a decided increase in the disturbance, which had dwindled; commencement of slow oscillation $8^h 44^m 51^s$, maximum about $9^h 3^m$.

Summarising the above abstracts we obtain the following times, in minutes after 8^h A.M.

Locality.	1st phase.	2nd phase.	3rd phase.	
			Commencement.	Maximum.
Nicolaiew . . .	17.0	30.0	—	—
Strassburg . . .	17.8	29.9	—	—
Shide	23.1	31.8	57.1	64.4
	—	31.7	56.8	—
Rocca di Papa . .	—	31.0	60.0	64.0
	—	—	55.0	64.0
	21.0	32.5	59.5	64.0
	21.0	31.5	58.5	64.0
Rome	21.2	31.2	58.3	64.2
	—	29.9	58.7	63.9
Ischia	20.5	31.5	(49.7)	66.0
Catania	—	32.4	—	64.0
	21.8	32.5	(44.8)	63.0

The commencement of the slow undulations on the great seismograph of the Rocca di Papa at 8^h 40^m obviously represents a different phase to that accepted on the other records as the commencement of the third phase. The same may be said of the times at Catania and Ischia.

The time of commencement of the disturbance at Nicolaiew, 8^h 7^m, being practically identical with the time of origin, cannot refer to any of the phases here being dealt with, if it is to be connected with this earthquake at all.

Converting the times into intervals we get the following result :—

Arc degrees.	Locality.	1st phase.	2nd phase.	3rd phase.	
				Commencement.	Maximum.
72.7	Nicolaiew	10.0	23.0	—	—
82.5	Strassburg	10.8	22.9	—	—
83.8	Shide	16.1	24.8	50.1	57.4
		—	24.7	49.8	—
85.9	Rocca di Papa . . .	—	24.0	53.0	57.0
		—	—	48.0	57.0
		14.0	25.5	52.5	57.0
		14.0	24.5	51.5	57.0
85.9	Rome	14.2	24.2	51.3	57.2
		—	22.9	51.7	56.9
86.2	Ischia	13.5	24.5	—	59.0
88.2	Catania	—	25.4	—	57.0
		14.8	25.5	—	56.0

5. INDIA, June 12, 1897.

The epicentre of this shock was an area of about 300 kiloms. long and about half as broad; the centre of this area lay in about N. lat. 26°, E. long 91°, which may

be taken as the epicentre for the purpose of calculating distances. The time of origin was 11^h 5^m G.M.T., with a maximum error of not more than 0·5^m, and probably not more than half of this.

As the records have been discussed in my report on this earthquake ('Mem. Geol. Surv. Ind.,' vol. 29) it is not necessary to repeat the details here. The times are tabulated here on a slightly different principle to that adopted in the report, and some slight changes have been made where the times as finally determined and published in the 'Boll. Soc. Sismol. Ital.,' vol. 3, Part II., differ from those originally communicated to me. They are given in minutes after 11^h G.M.T.

Locality.	1st phase.	2nd phase.	3rd phase.	
			Commencement.	Maximum.
Potsdam . . .	(18·7)	—	—	—
Catania . . .	17·3	25·8	46·0	49·5
Ischia . . .	17·2	25·8	45·0	47·50
	17·2	25·0	45·0	47·4
	18·0	—	45·0	—
	17·4	26·0	—	(57·3)
Rocca di Papa .	16·8	26·5	46·5	47·6
	17·5	25·3	43·1	47·0
	18·0	26·0	41·8	47·1
Rome . . .	17·1	24·3	43·5	47·5
	17·3	25·3	43·1	47·0
Padua . . .	16·8	26·7	42·5	47·2
Siena . . .	17·0	26·0	46·0	48·0
Pavia . . .	18·8	—	45·7	—
Strassburg . .	18·5	—	—	—
Grenoble . . .	(19·1)	—	—	—
Edinburgh . .	18·0	28·0	—	—

The times of the second and third phases at the Rocca di Papa and Padua are taken from copies of the original traces, they do not appear in the accounts as printed in the 'Boll. Soc. Sismol. Ital.,' vol. 3, Part II. The time at Siena is taken from the account and photograph of the trace sent to me from that observatory. In the 'Boll. Soc. Sismol. Ital.,' it is printed as 7^m 48^s, probably a misprint; the time at Verona is there given as 8^m, also a probable clerical or printer's error.

The time of the maximum of the third phase on the N.—S. component of the three-pendulum instrument at Ischia, 57^h 3^m, is much later than any of the others. This may be due to the direction of its sway; a maximum of 4·5 millims. is recorded at 48·1^m, but is exceeded by that of 57·3^m which reached 8·4 millims. This record may be excluded from consideration.

The Grenoble and Potsdam records are so divergent from the others that they had best be excluded from consideration. They probably correspond more or less to the maximum of the first phase as registered on the Italian instruments.

The uncertainty of the response of light horizontal pendula with photographic registration to the early phases of the disturbance, as compared with the greater constancy of response on the part of the very heavy pendula used in Italy, is very marked in the case of this earthquake.

Converted into intervals these times become

Arc degrees.	Locality.	1st phase.	2nd phase.	3rd phase.	
				Commencement.	Maximum.
63·9	Catania	12·3	20·8	41·0	44·5
64·0	Ischia	12·2	20·8	40·0	42·5
		12·2	20·0	40·0	47·4
		13·0	—	40·0	—
		12·4	21·0	—	—
		11·8	21·5	41·5	42·6
64·0	Rocca di Papa . . .	12·5	20·3	38·1	42·0
		13·0	21·0	36·8	42·1
64·1	Rome	12·1	19·3	38·5	42·5
		12·3	20·3	38·1	42·0
64·5	Padua	11·8	21·7	37·5	42·5
65·3	Siena	12·0	21·0	41·0	43·0
66·4	Pavia	13·8	—	40·7	—
66·5	Strassburg	13·5	—	—	—
70·9	Edinburgh	13·0	23·0	—	—

6. JAPAN, August 5, 1897.

According to Professor MILNE the focus of this earthquake was practically the same as that of June 15, 1896. The time of origin is determined as 0^h 9·4^m.

The following times are taken from the detailed account in 'Boll. Soc. Sismol. Ital.,' vol. 4, Part II., except in the case of Shide, for which the authority is 'Brit. Assoc. Rep.,' 1898, p. 192.

Nicolaiew.—0^h 17^m commencement, 0^h 22^m increase of amplitude to 8 millims., 0^h 31^m trace disappears, 3^h 52^m end of disturbance.

Shide.—0^h 22^m 25^s commencement, preliminary tremors 30^m, duration over 3^h.

Padua.—0^h 24^m commencement, end towards 2^h 30^m.

Rome.—Grande sismom. ; 0^h 23^m 55^s commencement on N.E.—S.W. component, a maximum at 0^h 28^m 25^s, after which the disturbance decreases; a sudden increase at 0^h 34^m 35^s, a second maximum at 0^h 35^m 10^s; slow undulations commence at 0^h 53^m 45^s, maximum 1^h 8^m 45^s, end 2^h 44^m 15^s. On the N.W.—S.E. component: 0^h 24^m 45^s commencement, a sudden increase at 0^h 34^m 55^s, slow undulations commence towards 0^h 59^m 45^s, maximum 1^h 8^m 25^s.

Sismom. sotter ; N.E.—S.W. component: 0^h 24^m 20^s commencement, a maximum at 0^h 27^m 55^s, after which the disturbance nearly dies out, 0^h 59^m commencement of slow waves, maximum at 1^h 8^m 40^s, end at 2^h 28^m 30^s. On N.W.—S.E. com-

ponent, the earlier stages of the disturbance are very ill marked, 0^h 59^m commencement of the slow undulations, maximum between 1^h 3^m 56^s and 1^h 8^m 12^s.

Rocca di Papa.—Hor. pendula; E.—W: 0^h 24^m 52^s commencement, 0^h 35^m 20^s a maximum, 0^h 45^m another maximum; 1^h 0^m commencement of a group of great undulations, maximum 1^h 6^m 40^s, end 2^h 15^m; N.—S.: 0^h 34^m commencement, 1^h 0^m commencement of slow undulations, 1^h 8^m 10^s maximum.

Grande sismom.; E.—W: 0^h 32^m 10^s commencement, 0^h 45^m 10^s commencement of undulations of 7^s period 1^h 8^m 40^s maximum, end about 2^h; N.—S.: 0^h 32^m 40^s commencement, 0^h 45^m commencement of slow undulations of 7^s period, maximum 1^h 8^m 30^s, end 2^h 12^m.

Ischia.—Hor. pendula; N.—S.: 0^h 24^m 33^s commencement, 0^h 35^m 14^s slower oscillations, 0^h 55^m 18^s commencement of very slow oscillations, 1^h 9^m 30^s maximum, 3^h 12^m end; E.—W.: 0^h 24^m 49^s commencement, 0^h 33^m 20^s resumption, 0^h 35^m 22^s slower oscillations, 0^h 54^m 7^s commencement of very slow oscillations, 1^h 8^m 39^s maximum, 3^h 0^m end.

Catania.—N.E.—S.W. component; 0^h 24^m 53^s commencement, 0^h 35^m 4^s increase of movement, 0^h 42^m 3^s commencement of slow undulations, 1^h 8^m 38^s maximum, 3^h 3^m 26^s end; N.W.—S.E.: 0^h 24^m 35^s commencement, 0^h 53^m 49^s commencement of slow undulations, 1^h 11^m 5^s maximum, 3^h 5^m 2·8^s end.

Tabulating as before we obtain the following times, in minutes after 0^h, for the different phases of the disturbance:—

Locality.	1st phase.	2nd phase.	3rd phase.	
			Commencement.	Maximum.
Nicolaiew . . .	22·0	31·0	—	—
Shide	22·6	—	—	—
Padua	24·0	—	—	—
Rome	23·9	34·6	53·7	68·7
	24·7	34·9	59·7	68·4
	24·3	—	59·0	68·7
	—	—	59·0	65·0
Rocca di Papa .	24·9	(35·3)	60·0	66·7
	—	34·0	60·0	68·2
	—	32·2	(45·2)	68·7
	—	32·7	(45·0)	68·5
Ischia	24·5	(35·2)	55·3	69·5
	24·8	33·3	54·1	68·6
Catania	24·9	35·1	(42·0)	68·6
	24·6	—	53·8	71·1

This is a singularly complete record, almost as much so as that of the great earthquake of June 12, 1897, and is besides remarkable for the very well defined maximum of the great undulations. The time of commencement of the disturbance

at Nicolaiew, 0^h 17^m, if due to this earthquake appears to indicate a different phase of the disturbance from that here characterised as the first phase. The times for the second phase at Rocca di Papa (35.3) and at Ischia (35.2) are shown by the detailed description to refer rather to the maximum of this phase than to the commencement as registered on other instruments. The "maximum" at the Rocca di Papa at 45^m, the commencement of undulations of 7^s period at 45.2^m, and the commencement of the slow undulations of Catania (42^m) all appear to refer to an earlier movement of this phase than the other records.

Converted into time intervals, these times become

Arc degrees.	Locality.	1st phase.	2nd phase.	3rd phase.	
				Commencement.	Maximum.
74.2	Nicolaiew	12.6	21.6	—	—
85.0	Shide	13.2	—	—	—
85.1	Padua.	14.6	—	—	—
87.7	Rome	14.5	25.2	44.3	59.3
		15.3	25.5	50.3	59.0
		14.9	—	49.6	59.3
		—	—	49.6	55.6
87.7	Rocca di Papa . . .	15.5	—	50.6	57.3
		—	24.6	50.6	58.8
		—	22.8	—	59.3
		—	23.3	—	59.1
88.0	Ischia	15.1	—	45.9	60.1
70.9	Catania	15.4	23.9	44.7	59.2
		15.5	25.7	—	59.2
		15.2	—	44.4	61.7

7. TURKESTAN, September 17, 1897.

On August 15, 1897, an earthquake was felt in Turkestan, and two others of greater severity on September 17. These have been made the subject of a special study by Dr. AGAMENNONE.* In this the epicentre is supposed to have been the same for all three. As the first is not recorded from any other place except Tashkent, this must be regarded as uncertain, and the records will not be taken into consideration. The other two were felt at a number of places, with greatest severity at Jisak and Ura Tube, where the earthquake reached 8 degrees of the Rossi-Forel scale, while the most distant was Kasalinsk, some 800 kiloms. from Jisak.

The epicentre is taken by Dr. AGAMENNONE as being on the northern slope of the mountains south of Ura Tube and Jisak, and the great extent of country over which the earthquakes, which only reached 8 degrees of the Rossi-Forel scale at their epicentre, were felt, is attributed to the depth of the focus from the surface. It seems more reasonable to suppose that the epicentre lay in the western Tian Shan

* 'Bol. Soc. Sismol. Ital.,' vol. 4, Part I., 1898, pp. 120-123.

Mountains to the southwards of Jisak and Ura Tube, in a region from which information is unattainable. It may be taken as in about 39° N. Lat. and 68° E. Long. ; this will certainly be nearer the truth than assuming the position of Jisak as that of the epicentre, and may be taken as correct within a limit of error of 1° of arc.

For the time we have only the observations at Tashkent. According to the director of the observatory there, as quoted by Dr. AGAMENNONE, the times at Tashkent were $8^{\text{h}} 7^{\text{m}} 30^{\text{s}}$ P.M. and $10^{\text{h}} 15^{\text{m}} 22^{\text{s}}$ P.M. respectively. As the distance from the epicentre is about 320 kiloms., the time of origin of the shock would be about 2^{m} before its arrival at Tashkent, taking the rate of propagation as 3 kiloms. per second. This would give the G.M.T. times of origin as $15^{\text{h}} 28^{\text{m}}$ and $17^{\text{h}} 36^{\text{m}}$ respectively, times which may be taken as correct within one minute of error.

1st Shock of $15^{\text{h}} 28^{\text{m}}$.

Nicolaiew.— $15^{\text{h}} 40^{\text{m}}$ commencement, maximum at $15^{\text{h}} 45^{\text{m}}$, end at $16^{\text{h}} 24^{\text{m}}$.

Potsdam.— $15^{\text{h}} 44^{\text{m}}$ commencement, at 47^{m} a slight increase, at 50^{m} , another sudden increase and the trace disappears shortly after ; end about 17^{h} .

Ischia.—The horizontal pendula were disturbed as early as $15^{\text{h}} 15^{\text{m}} 12^{\text{s}}$, but this was evidently the same disturbance as affected the instrument at Catania. The first decided increase was at $15^{\text{h}} 42^{\text{m}} 33^{\text{s}}$ on the N.—S., and $42^{\text{m}} 36^{\text{s}}$ on the E.—W. component, they decrease after 3 minutes, and at $15^{\text{h}} 50^{\text{m}}$ the oscillations are irregular, but grow more regular and longer, reaching a maximum at about 16^{h} . It is not possible to make out from the description, whether there was a defined maximum, but probably not. End at $16^{\text{h}} 35^{\text{m}}$.

Catania.—The disturbance commenced at $15^{\text{h}} 15^{\text{m}} 50^{\text{s}}$ on the N.W.—S.E. component, and at $15^{\text{m}} 15^{\text{s}}$ on the N.E.—S.W. ; this is some 13 minutes before the time of origin of the shock, and this disturbance must be attributed either to some other earthquake, or to tremors of a character which were not felt within the seismic area. In either case they cannot be referred to any of the three phases under discussion.

At $15^{\text{h}} 42^{\text{m}} 53^{\text{s}}$ on the N.W.—S.E., and at $42^{\text{m}} 47^{\text{s}}$ on the other component the disturbance becomes well marked. No definite phases are referred to but the maximum departure from normal was attained at $16^{\text{h}} 0^{\text{m}} 50^{\text{s}}$ on the N.W.—S.E., and at $16^{\text{h}} 1^{\text{m}} 0^{\text{s}}$ on the N.E.—S.W. component. End at $16^{\text{h}} 14^{\text{m}} 7^{\text{s}}$ on N.W.—S.E., and at $16^{\text{h}} 13^{\text{m}} 27^{\text{s}}$ on N.E.—S.W. component.

Rocca di Papa.—Grande sismom. ; commencement of disturbance at $15^{\text{h}} 50^{\text{m}}$ on E.—W., 52^{m} on N.—S. component. The horizontal pendulum commenced at $15^{\text{h}} 50^{\text{m}}$ on the N.—S. component. Maximum from $15^{\text{h}} 55^{\text{m}}$ to 58^{m} , end at $16^{\text{h}} 5^{\text{m}}$. The record of the other component shows nothing.

Rome.—The sismom. medio. showed at $15^{\text{h}} 38^{\text{m}} 30^{\text{s}}$ some minute undulations and nothing more till $47^{\text{m}} 30^{\text{s}}$. A small isolated group appears later with a maximum at $16^{\text{h}} 2^{\text{m}} 10^{\text{s}}$.

Edinburgh.—Slight disturbance of the bifilar pendulum from 15^h 55^m to 16^h 5^m.

Shide.—15^h 59^m 58^s commencement of disturbance lasting 40 minutes. Preliminary tremors 8 minutes.

These times are tabulated below, being given in minutes after 15^h.

Locality.	1st phase.	2nd phase.	3rd phase.	
			Commencement.	Maximum.
Nicolaiew . . .	—	40·0	45·0	—
Potsdam . . .	—	44·0	50·0	—
Ischia . . .	—	42·5	—	60·0
	—	42·6	—	60·0
Catania . . .	—	42·9	—	60·8
	—	42·8	—	61·0
Rocca di Papa .	—	—	50·0	—
	—	—	52·0	—
	—	—	50·0	58·0
Rome . . .	38·5	—	—	62·2
Edinburgh . . .	—	—	55·0	—
Shide . . .	—	—	60·0	68·0

The increase in the displacement of the horizontal pendulum at Potsdam, 47^m, does not seem attributable to any of the three phases under consideration.

2nd Shock of 17^h 36^m.

Nicolaiew.—18^h 2·5^m commencement of disturbance, end at 18^h 57^m.

Potsdam.—17^h 51·5^m commencement; at 55·5^m there is a sudden increase of amplitude, and the trace becomes lost shortly afterwards. End at 19^h ½^h.

Ischia.—The horizontal pendula were disturbed at 17^h 36^m 58^s, or practically simultaneously with the origin of the shock. As in the case of the previous earthquake, and for the same reasons, this disturbance may be neglected. At 44^m 35^s on the N.—S. pendulum there was a slight increase, and at 46^m 10^s on the other a group of eight oscillations of 3·4^s period. At 50^m 40^s the disturbance of the N.—S. pendulum was more noticeable, afterwards diminishing, and at 51^m on the other is a group of undulations of 6^s period. At 54^m on the one and 54^m 30^s on the other the oscillation was more noticeable and slow. At 18^h 0^m it was very slow, but irregular, reaching its maximum at 18^h 5^m, and ceasing at 18^h 51^m.

Catania.—Commencement about 17^h 46^m 18^s of very minute undulations; from 17^h 51^m 55^s to 52^m 37^s a group of seven very regular undulations of 6^s period end at 19^h 11^m 1^s. On the other (N.E.—S.W.) component the time of commencement is the same; the end is at 18^h 0^m 48^s.

Rocca di Papa.—Grande sismom. Commencement of slight oscillations at 17^h 48^m, which have an easily distinguished maximum at 18^h 6^m, and end at 19^h 17^m. The

horizontal pendula commenced to oscillate at 17^h 58^m; no marked maximum; end 18^h 10^m.

Rome.—Sismom. sotter. At 17^h 45^m 50^s \pm 5^s the seismograph was disturbed; the disturbance decreased, but became once more recognisable at 52^m.

Edinburgh.—18^h 2^m to 18^h 12^m slight disturbance on bifilar pendulum.

Shide.—17^h 59^m 58^s commencement of disturbance, lasting 38^m. Preliminary tremors lasted 8^m.

Summarising these times we get the following, the times being tabulated in minutes after 17^h:—

Locality.	1st phase.	2nd phase.	3rd phase.	
			Commencement.	Maximum.
Nicolaiew . .	—	—	(62·5)	—
Potsdam . . .	—	51·5	—	—
Ischia, N—S .	(44·6)	50·7	60·0	65·0
E—W .	46·2	51·0	—	—
Catania . . .	46·3	51·9	—	—
Rocca di Papa .	—	—	—	66·0
" . . .	—	—	58·0	—
Rome	45·8	52·0	—	—
Edinburgh . .	—	—	62·0	—
Shide	—	—	60·0	68·0

The maximum at Shide is put at 8^m after the commencement, the recorded duration of the preliminary tremors.

The time of commencement of slight oscillations on the grande sismometrografo at the Rocca di Papa is not included, as it falls intermediate between the times of the first and second phases, and cannot be recognised as a distinct phase on any other instrument.

The time of commencement at Nicolaiew, as compared with other places, is decidedly late. The instrument does not appear to have commenced to work till a phase more closely corresponding to the maximum, than the commencement of the long period waves.

Besides the phases included in the table, there seems to be another, corresponding to the increased disturbance at 17^h 54^m and 54^m 30^s at Ischia, and at 17^h 55·5^m at Potsdam.

With these exceptions the times of commencement or of sudden increase of the disturbance exhibit a very close concordance, the most serious divergence being the time of commencement on the N.—S. pendulum at Ischia. As this instrument showed tremors continuously from 17^h 36^m 58^s, and the time given is that of a feeble augmentation, it may well be somewhat in error owing to the difficulty of determining

the exact time of this commencement. The better marked group of waves on the E.—W. pendulum record seem to afford a more trustworthy time, and the other will be discarded.

Distinguishing the two shocks as (1) and (2) respectively, we get the following table of time intervals in minutes :—

Arc degrees.	Locality.	1st phase.	2nd phase.	3rd phase.	
				Commencement.	Maximum.
27·5	Nicolaiew . . (1) . .	—	12·0	17·0	—
39·9	Potadam . . (1) . .	—	16·0	22·0	—
	(2) . .	—	15·5	—	—
41·0	Ischia . . (1) . .	—	14·5	—	32·0
	(2) . .	—	14·6	—	32·0
	(2) . .	—	14·7	24·0	29·0
	(2) . .	10·2	15·0	—	—
42·4	Catania . . (1) . .	—	14·9	—	32·8
	(2) . .	—	14·8	—	33·0
42·5	Rocca di Papa (1) . .	10·3	15·9	—	—
	(2) . .	—	—	22·0	—
	(2) . .	—	—	24·0	—
	(2) . .	—	—	22·0	—
	(2) . .	—	—	—	30·0
	(2) . .	—	—	22·0	—
42·5	Rome . . (1) . .	10·5	—	—	34·2
	(2) . .	9·8	16·0	—	—
48·8	Edinburgh . (1) . .	—	—	27·0	—
	(2) . .	—	—	26·0	—
48·9	Shide . . (1) . .	—	—	32·0	40·0
	(2) . .	—	—	24·0	32·0

§ 3. From the details given above it will be seen that of the eleven shocks, grouped as seven earthquakes, which satisfied the conditions laid down, all gave threefold records similar to that of the Indian earthquake of 1897. This, however, would not of itself prove the correctness of the interpretation suggested in that case, nor even that the three phases referred in each case to the same form of wave motion. To do this it must be shown firstly that the intervals of time and space bear, in each case, such relation to each other as will show that the three phases recognised refer to the same forms of wave motion, and, secondly, that the forms of wave motion to which they refer are those to which they have been assumed to be due.

In carrying out this comparison it will be convenient to group and average the observations in the case of each earthquake, not only in the case of each station, but in each group of stations separated from the origin by approximately the same arc. The limit taken will be 5° , and the records from each group of stations lying within this limit will be averaged. An exception will, however, be made in the case of the instruments with photographic registration; these, in spite, or perhaps because, of

their great sensitiveness to minute tilts, do not seem so well adapted for picking up and recording the wave motion represented by the first and second phases. To whatever cause this may be due, the records printed above show that, with regard to these phases, they do not respond with the same constancy or concordance as the heavy weighted pendula favoured in the Italian observatories.

Taking the records of the first phase motion, and separating the records of the heavy pendula with mechanical record from the light photographic pendula, we get the following results :—

First Phase ; heavy pendula.

Earthquake No.	Arc degrees.	No. of observations.	Interval. Minutes.	Rate. Kiloms. per second.	Locality.
7	42.1	4	10.2	7.6	Italy.
5	64.2	13	12.4	9.6	"
1	85.2	5	14.8	10.6	"
4	86.3	5	14.1	11.3	"
3	86.5	4	15.8	10.1	"
6	88.1	9	15.1	10.8	"
3	90.9	1	16.2	10.4	Catania.
2	102.8	1	17.6	10.8	Rome.

Here there will be noticed a close accordance in the time intervals and the apparent rate of transmission, both of them increasing as the distance from the origin increases, but not in the same ratio. The only break of any significance in the regular increase is in the case of earthquake No. 4, and even this becomes unimportant when it is remembered that the uncertainty of the exact time and place of origin, combined with the shortness of the interval, may produce an error in the calculated rate of time amounting to nearly 1 kilom. per second.

The photographic records show a greater irregularity, but the general result is the same, as may be seen from the following tabular statement :—

First Phase ; light pendula.

Earthquake No.	Arc degrees.	No. of observations.	Intervals. Minutes.	Rate. Kiloms. per second.	Locality.
5	66.5	1	13.5	9.0	Strassburg.
1	70.1	2	12.6	10.3	Russia.
5	70.8	1	13.0	10.0	Edinburgh.
4	72.7	1	10.0	13.5	Nicolaiew.
6	74.2	1	12.6	10.9	"
4	82.5	1	10.8	14.1	Strassburg.
4	83.8	1	16.1	9.6	Shide.
6	85.0	1	13.2	11.9	"
2	120.9	1	18.6	12.0	Charkow.

Turning to the second phase, we see the same features repeated, and as the time intervals are longer, and consequently the effect of a small error less, there is a still more marked steadiness in the increase of apparent velocity with distance, as is shown in the following tabular statements :—

Second Phase ; heavy pendula.

Earthquake. No.	Arc degrees.	No. of observations.	Interval. Minutes.	Rate. Kiloms. per second.	Locality.
7	41·7	8	15·0	5·1	Italy.
5	64·2	11	20·7	5·7	"
1	85·2	4	25·2	6·3	"
4	86·5	8	24·6	6·5	"
3	87·9	6	25·7	6·3	"
6	88·2	7	24·4	6·7	"
2	102·8	1	25·2	7·5	Rome.

Second Phase ; light pendula.

Earthquake. No.	Arc degrees.	No. of observations.	Interval. Minutes.	Rate. Kiloms. per second.	Locality.
7	27·5	1	12·0	4·2	Nicolaiew.
7	39·9	2	15·7	4·7	Potsdam.
1	70·1	3	24·8	5·2	Russia.
5	70·8	1	23·0	5·7	Edinburgh.
4	72·7	1	23·0	5·8	Nicolaiew.
6	74·2	1	21·6	6·4	"
4	82·5	1	22·9	6·7	Strassburg.
4	83·8	2	24·7	6·3	Shide.
2	117·6	1	27·1	8·0	Nicolaiew.

Turning to the third phase and taking first the times at which the slow movement was recognised as commencing, we get a much less closely concordant series of times than in the case of the first or second phase. The interval being also longer, these divergences have but a small influence on the deduced rate of travel, nor do the extreme values depart much from the average value, except in the case of those records which have been rejected as too much in advance of the others to allow of their reference to the same phase.

The average of the observations works out as follows :—

Third Phase. Commencement.

Earthquake. No.	Arc degrees.	No. of observations.	Interval. Minutes.	Rate. Kiloms. per second.	Locality.
7	27.5	1	17.0	3.0	Nicolaiew.
7	41.8	6	22.7	3.4	Europe.
7	48.8	4	27.2	3.3	England.
5	64.3	12	39.8	3.0	Italy.
1	71.5	3	38.8	3.4	Russia.
4	83.8	2	50.0	3.1	Shide.
1	85.1	3	45.3	3.5	Italy.
4	85.4	8	51.0	3.1	"
6	88.1	9	47.8	3.4	"
2	102.6	4	54.1	3.5	"

Here we get a result different from that obtained in the case of the first and second phases, in that the time intervals increase in practically the same ratio as the distances, and there is no indication of an increase of apparent velocity with the distance. The irregularity in the values of the rate of propagation is easily explicable by the difficulty of obtaining an accurate record of the commencement of this phase of motion. Whatever may be the manner of propagation of this form of wave motion, it seems to manifest itself in much the same manner as the ripples which radiate over the surface of a pond. There is a band of larger and distinctly visible ripples, and as these radiate they come to be preceded and followed by an ever widening belt of longer and flatter wavelets whose limits cannot be determined on account of the gradual manner of their decrease in height. In a similar manner the surface undulations which form the last phase of a distant earthquake commence as very long and flat waves, gradually increasing in height, and the exact moment at which these will begin to influence an instrument may be materially delayed or advanced by very slight differences in its sensitiveness.

This may be illustrated by taking the maximum and minimum values for the rate of travel given by the records averaged in the table given above. They are

Earthquake. No.	Mean arc.	Rate of travel. Kiloms. per second.	
		Maximum.	Minimum.
7	41.8	3.6	3.2
7	48.8	3.8	2.8
5	64.3	3.2	2.8
1	75.3	3.5	3.3
4	85.4	3.3	3.0
3	87.3	3.7	2.9
6	88.1	3.8	3.2
2	102.7	3.8	3.2

Here there are evidently very great divergences, which can only be attributed to differences in the sensitiveness of the instruments to this phase. There is no visible relation between distance and rate of travel, while the apparent rates vary from 3·2 to 3·8 kiloms. per second.* In view of these divergences it becomes a question whether some of the records rejected as giving times much too early should not be included, and for this reason they have been tabulated here.

Earthquake. No.	Arc degrees.	Interval. Minutes.	Rate. Kiloms. per second.	Locality.
7	39·9	19·0	3·9	Potadam.
7	41·0	18·0	4·2	Ischia.
4	85·9	33·0	4·8	Rocca di Papa.
4	86·2	42·7	3·7	Ischia.
6	87·7	35·6	4·5	Roca di Papa.
3	88·0	35·2	4·6	Ischia.
4	88·2	37·8	4·3	Catania.
3	90·9	38·0	4·4	"
6	90·9	32·6	5·1	"
2	103·0	43·0	4·4	Ischia.

From this, if the data are accepted, it seems that the first waves of this phase may travel at rates that rise to near 5 kiloms. per second, though those which are ordinarily registered at the commencement of this phase have not a greater apparent rate of travel than about 3·5 kiloms. per second.†

If, instead of the very indeterminate commencement of this phase, we take the more easily determinable time of the maximum movement, we find, as shown in the table below, that greater uniformity of result which might be expected to follow from the fact that the recorded times are less influenced by variations in the sensitiveness of the different instruments.

* The minimum values may be neglected, as they are evidently due to a tardiness in action of the instruments.

† The Sacramento earthquake of April 19, 1892, recorded at Strassburg, gives a rate of 3·8 kiloms. per second over an arc of 82·5°. The Venezuela shock of April 28, 1894, recorded in Russia, gives 3·5 and 4·0 kiloms. per second over arcs of 93·8° and 93·6° respectively. The earlier phases of these shocks were not recorded.

Third Phase; maximum.

Earthquake No.	Arc degrees.	No. of observations.	Interval. Minutes.	Rate. Kiloms. per second.	Locality.
7	41·8	7	31·8	2·4	Italy.
7	48·8	2	35·0	2·6	Shide.
5	64·2	10	43·1	2·8	Italy.
1	72·9	1	46·0	2·9	Nicolaiew.
1	84·9	3	56·7	2·8	Italy.
3	88·0	12	53·8	3·0	"
6	88·3	12	59·0	2·8	"
2	102·8	4	67·8	2·8	"

Here, if we exclude the results of the Turkestan earthquake of 1897, there is a most striking concordance in the rates of transmission at all distances between 60 and 120 degrees of arc. The lesser velocity in the case of the smaller arc will be considered further on; here it will be enough to say that in itself this cannot be regarded as an indication of a progressive increase of apparent rate of propagation with distance, such as was observed in the case of the first and second phases.

§ 4. Before proceeding further with this investigation it will be necessary to hark back and consider some general principles involved.

Firstly, the rate of propagation may, as is well known, mean one of two things, either (1) the apparent rate of propagation as measured at the surface of the earth, or (2) the true rate of propagation as measured along the actual wave path. These velocities, whose distinction is well recognised and for which distinct symbols are always employed, must, however, be further subdivided, and for the present purpose the four following values recognised:—

v = the apparent rate of propagation at any given point on the surface. This is what is commonly meant by apparent rate of propagation.

v_a = the apparent average rate of propagation as between two points on the surface of the earth. The only average which appears to be of any value is that referred to the origin. It is this value which has been given in the tabular statements above as the rate.

V = the true rate of propagation at any given point of the wave path.

V_a = the true average rate of propagation, obtained by dividing the distance, measured along the wave path, by the time interval.

In the special case of waves propagated along the surface with a uniform velocity these four values are identical; if wave motion is propagated at a uniform speed and along rectilinear paths through the earth the values of V and V_a will be identical but different from v and v_a , which will also differ from each other. In any other case the four quantities must necessarily be different.

The earliest suggestion that the propagation of earthquake movement was along curved, and not straight, wave paths is contained in a paper by Dr. A. SCHMIDT,* of Stuttgart, in which he pointed out that the assumption, made by all previous investigators, of a constant rate of propagation and a rectilinear wave path, was an improbable one. The very different conditions of temperature and pressure in the interior of the earth cannot be without influence in modifying the elasticity and consequently the rate of propagation, and an investigation of the observed rates of propagation of certain earthquakes indicates that this modification results in an increase of the rate of propagation with the depth below the surface.

The problem has been investigated mathematically by M. P. RUDZKI,† for the case of a spherical body, such as the earth. He shows that the wave path which would be straight in the case of a homogeneous solid, or one in which the rate of transmission was constant for all distances from the centre, would be convex towards the centre if the velocity of transmission increased as the distance from the centre diminished, that is as the depth below the surface increased, and concave towards the centre if the opposite were the case. He then investigates the form of the wave paths on the assumption that the velocity of propagation is a constant function of the radial distance from the centre.

On this supposition he finds that the wave paths would form a series of curves intersecting at the focus, the upward path to the surface forming part of the same curve with the path of the wave motion which starts downwards from the focus in the opposite direction. Each of these curves is symmetrical on either side of a radius, drawn from the centre of the earth, which intersects the curve at the point where it approaches nearest to the centre of the earth, and where it is tangent to a circle drawn round this centre. A limiting condition is found where this radius passes through the focus; in this case the curves are symmetrical on either side of the focus, and the circle on which this group of curves intersects the surface of the sphere is taken as the limit between an inner and an outer area.

Turning from the wave paths and the variations in V , or the true velocity, he then deals with the variations of v , or the apparent velocity at the surface. This is infinite at the seismic vertical, and decreases outwards till the limit of the inner area is reached, where it has its minimum value. Passing from this inner area into the outer area, the value of v increases once more, and becomes infinite at the antipodes of the seismic vertical.

It is only the value of v which is investigated, but it is obvious that the value of V , or the apparent average velocity of transmission from the centre, must be subject to similar variations. It can never be infinite, but within the inner area it will

* "Wellenbewegung und Erdbeben. Ein Beitrag zur Dynamik der Erdbeben." 'Jahresheft Ver. f. Vaterland. Naturk. in Württemberg,' vol. 44, 1888, pp. 248-270.

† "Ueber die scheinbare Geschwindigkeit der Verbreitung der Erdbeben" (German translation of paper in Polish, published by the Academy of Krakau). GERLAND'S Beiträge z. Geophysik, vol. 3, 1888, pp. 485-518.

decrease, and within the outer area increase, as the distance from the epicentre increases.

The depth of the focus is always so small in comparison with the diameter, and the size of the inner area so small in comparison with the surface, of the earth, that they may be left out of consideration in a study of the propagation of earthquake motion to great distances. Consequently we should find, if the disturbance is transmitted through the earth, an increase in the apparent rate of transmission with an increase in distance from the origin. This apparent rate of increase will be proportionate to the ratio between arc and chord if the wave motion is propagated in straight lines, it will be less if the rate of propagation diminishes with the depth and the wave paths are concave towards the centre, and greater if they are convex, and the rate of propagation increases with the depth.

It must further be noticed that the regularity of increase of v and v_0 with the distance from the origin only holds good if the increase of V is a constant function of the distance from the centre of the earth. This may reasonably be expected so long as there is no great change in the character of the medium traversed and the change in the elastic constants is principally due to the increase of temperature and pressure. It is, however, very probable that the central core of the earth is metallic, composed principally of native iron, surrounded by an outer shell of magma, which would be stony or glassy in a cooled and solidified form. If this be the case the wave on passing from the one to the other would enter a medium in which the change of elasticity due to temperature and pressure would be complicated by an initial difference in the elastic constants.

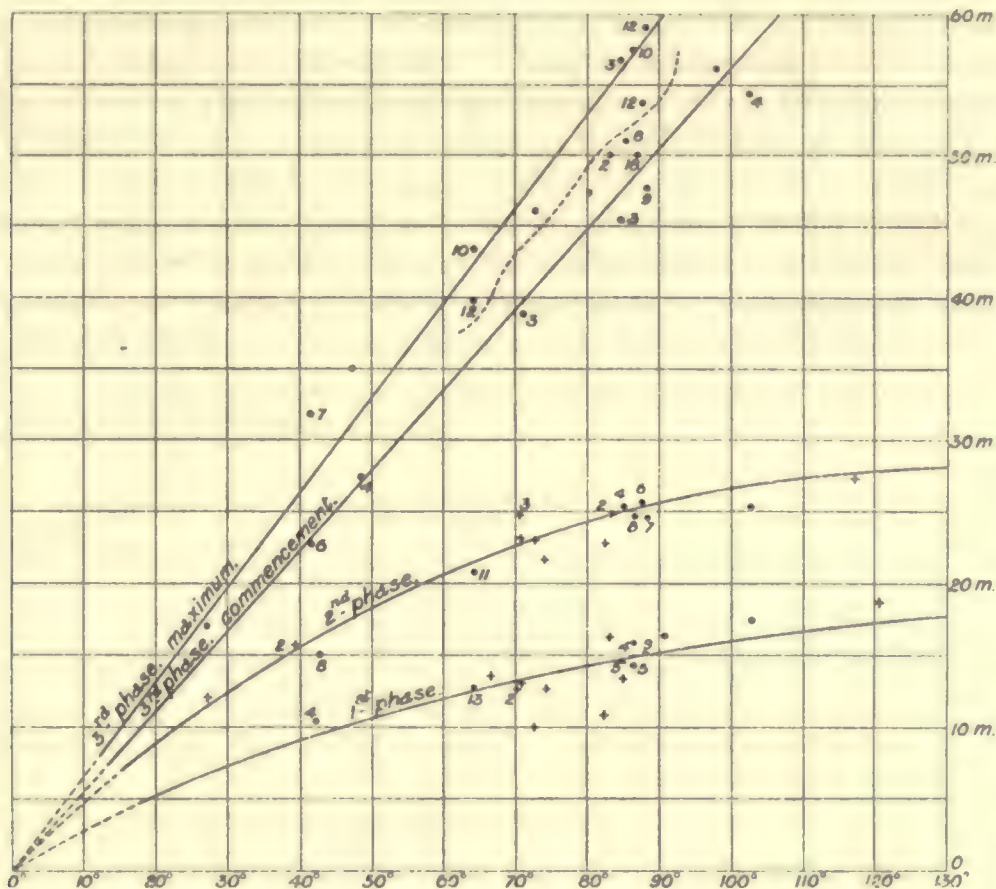
If, as is probable, there should be a sudden increase of V when the wave path enters the central core, it is possible that v might become infinite along a circle removed from the antipodes of the origin, and beyond that have a negative value. That is, it is conceivable that the disturbance might emerge at the antipodes before it reached the surface at some point nearer the origin. In any case a sudden change in the rate of increase would exhibit itself as an interruption of the regular curvature of the time curve, this being bent downwards if the change was an increase, upwards if it was a decrease, of the regular rate of increase of velocity with depth below the surface.

Turning to the application of these general principles to the recorded observations, this seems to be most conveniently effected in the graphic manner employed in the accompanying diagram. On this the recorded times of the first, second, and third phases have been plotted against their distances from the origin in degrees of arc, and smoothed curves drawn through them.

It may not be amiss to repeat here that in obtaining these times no selection was exercised. The times of commencement and of any marked change of amount or character of movement were taken from the published record, and the only subsequent selection made was the rejection, in those cases only which have been specially

mentioned, of records of individual instruments which were markedly divergent from those of others whose times were in close concordance with each other. To have included these in the general average would not have led to greater, but to less, accuracy in the result.

As, moreover, the light horizontal pendula do not seem to respond with the same consistency to the motion of the first two phases, as the heavily weighted pendula used in Italy, their records have been distinguished on the plate, being indicated by a



Time curves of the three phases of earthquake motion recognisable in distant records.

cross, while the records of the Italian instruments are plotted as circles. A small figure against either cross or dot means that it is the average of a corresponding number of not very divergent instrumental records; where no figure is entered only a single instrumental record is indicated.

In the case of the third phase there was no reason for distinguishing between the records of the two types of instruments, but by far the preponderating number of records have been obtained from the Italian instruments. Generally when a light pendulum with photographic record is affected by one of the first two phases, the movement of the pendulum is so great in the third phase that the swing of the spot

of light passes the limit of photographic registration, and the record is lost. These remarks do not apply to Professor MILNE's pattern of instrument, where the displacement of the pendulum is directly photographed without any reflection or magnification of the movement, but, as the time of maximum displacement is not to be found in the published accounts of the records of this instrument, it has not been possible, except in a few cases, to utilise the Shide records.

The two types of instrument differ not only in detail but in the object aimed at in their construction; HORACE DARWIN's bifilar pendulum, as well as the horizontal pendula of REBEUR-PASCHWITZ, GERLAND and MILNE, were designed to register tilting, and are not primarily intended to respond, by their inertia, to a rapid movement of the ground in a horizontal direction. The heavily weighted pendula are, on the contrary, intended to respond to horizontal shakes, the heavy mass acting as a steady point. Professor GRABLOWITZ has shown,* from a comparison of the records of the instruments at Ischia, which are under his charge, that during the first phase the record is due mainly to inertia, and only to a small extent, if at all, to tilting, while in the latter stage the opposite takes place, and the record is principally due to tilting. The greater constancy of record of the heavy pendula in the case of the first phase, and the greater sensitiveness of the light pendula to the motion of the third phase are, consequently, in accordance with the objects specially aimed at in the construction of each type of instrument.

§ 5. Taking up the consideration of the records of the first two phases, it will be seen that, as plotted on the diagram on page 163, they all lie very close to two curved lines, starting from the origin and proceeding with a regularly decreasing curvature—at any rate to a distance from the origin of 90° of arc. In both cases the only serious divergence of a record from the curve is in a few cases of photographic records, and this is most marked in the case of the first phase. The concordance is so close that the curves drawn may be taken as, in the main, representing the true time curves† of these two phases.

From the construction of these curves they represent graphically the apparent velocity at any point, for this is directly proportional to the cotangent of the angle of inclination. The relation of the apparent velocity to distance is consequently exactly what is required on the assumption that the wave motion is transmitted through the earth, and a simple calculation shows that the increase is markedly greater than what would be due to rectilinear propagation. It follows, therefore, that for the wave motion represented by these two phases, the rate of propagation increases with the depth, and the wave paths are convex towards the centre of the earth.

* 'Boll. Soc. Sismol. Ital.,' Part II, *passim*. Professor GRABLOWITZ only recognises two phases, corresponding to the first and third of this paper.

† Dr. A. SCHMIDT has proposed ('Jahresheft Ver. f. Vaterland. Naturk. in Württemberg,' vol. 44, 1888), to apply the term "hodograph" to these time curves, but as this term is already used in a very different sense, I think it best to abandon the word, and use the simple expression "time curve."

Having thus two forms of wave motion propagated through the earth, it is natural to regard them as condensational and distortional, and this inference is strengthened if we complete the curves and carry them on to the origin. They then give initial velocities of transmission of about 5 and 3 kiloms. per second respectively.

Little is known of the rate of transmission of elastic waves through rock. Direct experimental determinations, by measuring the rate of transmission of the disturbance set up by an explosion, give little assistance, as the velocities obtained are much less than should result from the elastic constants of the rock, a difference probably due to the weathered and fissured condition of all rocks near the surface. The only experiments of much value are those of Professor GRAY and MILNE,* who measured the elastic constants of certain rocks, and obtained results from which the following rates of transmission of condensational and distortional waves were deduced :—

	Condensational.	Distortional.	Ratio.
Granite	3.95	2.19	1.80
Marble	3.81	2.08	1.83
Slate	4.51	2.86	1.58
Mean	4.09	2.38	1.68

The original records of the experiments have been lost, and some doubts attach to the absolute correctness of the results,† but they are probably not seriously in error.

In Professor KNOTT's paper‡ the same experiments are referred to, but the elastic constants differ slightly from those published in the 'Quarterly Journal.' Combining them with the densities as given by Professor MILNE we get—

	Condensational.	Distortional.	Ratio.
Granite	4.2	2.3	1.8
Marble	4.0	2.2	1.7
Slate	4.7	3.0	1.4
Mean	4.3	2.5	1.7

From the above we may conclude that the rates of transmission of elastic waves through continuous rock such as is met with at a little distance from the surface,

* 'Quart. Jour. Geol. Soc.,' vol. 39, 1883, p. 140.

† 'Seismol. Jour.,' Japan, vol. 3, 1894, p. 87.

‡ 'Trans. Seismol. Soc.,' Japan, vol. 12, 1888, p. 118.

in other words, the initial velocity of propagation in the case of an earthquake, is not far removed from 4.5 kiloms. per second in the case of condensational, and 2.6 kiloms. per second in the case of distortional waves.

These values are in close accord with the ones obtained from the curve given by distant observations, the difference being no greater than might easily be made to vanish by a slight manipulation of the extrapolated portion of the curve. We may consequently adopt the conclusion that the first phase represents the arrival of condensational, and the second that of distortional waves, which have travelled through the earth from the origin to the place of record.

§ 6. If the curves drawn on the diagram represent the true time curves, it should be possible to deduce from them the relation between the variation of velocity of transmission and depth below the surface. Until a larger number of observations have been collected, and it is certain that the true curve does not exhibit irregularities, not shown by the few records as yet available, it does not seem advisable to attempt this; but a tentative investigation of the results obtained at a distance of 85° , where, owing to the number of observations available, the curves are fixed with great certainty, will not be unprofitable.

For a distance of 85° , or about 9,500 kiloms. from the origin, the time intervals are very close to 15^m and 25^m respectively. These intervals give apparent mean velocities of 10.5 kiloms. and 6.3 kiloms per second, and as the wave path is a curve convex towards the centre of the earth, these are probably nearer the true average velocities than the mean apparent velocities as measured along the chord, which are 9.5 kiloms. and 5.7 kiloms. per second respectively.

The maximum velocity is necessarily greater than the mean, and we shall probably be not far wrong in assuming that the maximum excess over the initial velocity is about double the mean excess. To be on the safe side the apparent mean velocities as measured along the chord may be taken; here the mean excess is 5.0 kiloms. and 3.1 kiloms. per second respectively. Adding the doubles of these to the initial velocities of 4.5 and 2.6, we obtain a maximum velocity of 14.5 kiloms. per second for the condensational, and 8.8 kiloms. per second for the distortional waves respectively.

If we put V_i for the initial velocity, and V_m for the maximum, then

$$V_i/\sin \alpha_i = V'/\sin \alpha' = V''/\sin \alpha'' = V_m/\sin \alpha_m,$$

where α_i is the initial angle of incidence, or what may be called the plunging angle at which the particular ray or wave path leaves the focus, and α_m is the angle of refraction where the maximum velocity is attained. But α_m is necessarily 90° , the maximum velocity being attained where the wave path is tangent to a circle drawn round the centre of the earth. Hence

$$V_i/V_m = \sin \alpha_i.$$

Applying this formula, we find that for the condensational wave α , is $18^\circ 10'$, and for the distortional $17^\circ 10'$. Measuring these angles from the horizontal instead of the vertical, they become $71^\circ 50'$ and $72^\circ 50'$ respectively.

Assuming that the true wave path is an arc of a circle, it is easy to calculate the depth reached by the wave path. For a condensational wave it is close on 2,800 kiloms. The value in the case of the distortional wave is practically the same, though slightly higher.

From this it follows that the disturbances registered in Europe as the first and second phases of earthquakes which originate in Japan, are due to wave motion which, at the origin, has plunged downwards at an angle of about 72° with the horizon, and has penetrated to a depth of about 3,000 kiloms. from the surface, or to about 0.55 of the radius as measured from the centre.

As to approximate indication, the corresponding values for 30° and 60° may be given.

	30° .	60° .	85° .
Plunging angle	65°	69°	72°
Maximum velocity (kilom. per sec.) . . .	10.0	12.5	15.0
Maximum depth from surface (kilom.) . .	1000	2000	3000

These results do not pretend to accuracy, but at any rate they indicate the order of magnitude of the true figures, and indirectly point to the cause of the feebleness of the disturbance due to these waves at a distance from the origin. It will be seen that the waves which are spread over the whole surface of the earth, outside a circle of 30° radius round the origin, are those contained within a cone of 50° apical angle at the origin, that is to say, about $\frac{1}{20}$ th of the total energy of the shock is distributed over $\frac{1}{20}$ ths of the surface of the earth.

It will not be without interest to form some idea of the elastic constants at the depth reached by the waves of Japanese earthquakes on their path to Europe. Taking the velocities of 14.5 and 8.8 kiloms. per second, and an assumed density of 3.5, the wave modulus of elasticity is

$$m = 5.86 \times 10^{12} \text{ for the condensational wave,}$$

$$n = 2.16 \times 10^{12} \text{ for the distortional wave.}$$

Here n is the rigidity, and putting $m = k + \frac{2}{3}n$, where k is the bulk modulus, we get the result

$$k = 4.24 \times 10^{12} = \text{bulk modulus.}$$

Comparing these values with those of granite, as given in Professor KNOTT'S

paper, we find that the rigidity is 15 times, and the bulk modulus nearly 12 times, greater than that of granite. If instead of a density of 3·5 we assume the more probable density of 7·0, these values would have to be further increased by about one-half, and would become 17 and 21·5 times the corresponding constants for granite.

According to RUDZKI,* if the wave paths are circular arcs, the function of the radial distance which represents the velocity of transmission takes the form

$$V = A - Br^2.$$

Taking the value of V to be 14·5 kiloms. per second at a distance of 0·55 of the radius, and equating this with the assumed initial velocity of 4·5 kilom. per second, we get

$$V = 18·5 - 14r^2,$$

r being expressed as a fraction of the radius of the earth. For the distortional wave the formula becomes

$$V = 11·5 - 9r^2.$$

These formulæ give results in very fair accordance with those deduced from the observations recorded, but cannot be accepted as more than empirical approximations. They indicate that the maximum velocity of transmission at the centre of the earth should be about 18·5 kiloms. per second for the condensational, and 11·5 kiloms. per second for the distortional wave, if there is no sudden change in the increase of the elastic constants below the depth of 3,000 kiloms. from the surface.

It is, however, by no means certain that a regular increase of the elastic constants to the centre of the earth is to be looked for; on the contrary, a sudden change is to be looked for where the wave path leaves the outer stony shell to enter the central metallic core which may reasonably be supposed to exist.

Though we have no direct knowledge of the constitution of the interior of the earth, we do know not only its average density, but also approximately the rate of increase of density from the surface to the centre. The estimates of this, made by LAPLACE and WALTERSHAUSEN, give values for 0·5 and 0·6 of the radius as follows :—

	0·5	0·6
Laplace	8·23	7·25
Waltershausen . . .	7·85	7·08

* GERLAND'S 'Beiträge z. Geophysik,' vol. 3, 1898, p. 518

As the density of iron is about 7·5, and as its density in the interior of the earth is, on the one hand, lessened by increased temperature, and, on the other, increased by pressure, we may take it that the central metallic core extends to about 0·55 of the radius from the centre, or to about the same depth as is reached by the wave paths which emerge at a distance of 90° of arc from the origin.

It will be interesting to see if observations which may be obtained hereafter at distances of more than 90° of arc from the origin bear this out; at present we have only the few observations of the Argentine earthquake of 1894. If the Tokio record of this can be accepted as representing the arrival of the condensational waves, there is a marked fall in the time curve between 90° and 155°, indicating an earlier emergence of the waves at the greater as compared with the lesser distance.

The European records of the same shock do not indicate a drop in the time curve; those of the first phase lie very close to the continuation of the curve for the condensational wave, but to bring the second phase near the continuation of this curve it has to be bent downwards into greater parallelism with the time curve of the first phase, thus indicating a change in the ratio of the elastic constants. The observations are, however, too few for any dependence to be placed upon them.

§ 7. The records of the third phase show no such variation of velocity with distance from the origin as was noticed in the case of the first and second phases. The velocities of propagation as deduced from the times of commencement show a good deal of variation among themselves, but there is no indication of an increase of apparent rate of propagation with distance.

I have already referred to the difficulty there is in determining with certainty the time of commencement of this phase of wave motion, and if we turn to the time of maximum of this phase, usually determinable with greater certainty, we find a close agreement in the rate of propagation at all distances, except in the case of the Turkestan earthquakes and the shortest arcs dealt with. These are slightly but distinctly less than those deduced from observations over longer arcs, but with this exception the observations point to the conclusion that the apparent rate of propagation is uniform at all distances from the origin.

This conclusion is not in concordance with the latest results published by Professor MILNE,* who has deduced as average rates of propagation of the large waves the following values :—

Distance from origin.	20°	60°	80°	110°
Velocity of propagation, kiloms. per second	2·1	2·8	2·9	3·3

These values if plotted do not fall into a smooth curve, but such as it is the curve would point to propagation through the earth along brachistochronic paths, slightly concave towards the centre of the earth. If this be the case, the form of

* 'Brit. Assoc. Rep.,' 1898, p. 220.

wave motion is something very different to any which has yet been investigated, so far as I know, and requiring some form of wave motion whose rate of propagation decreases with an increase of the modulus of elasticity.

Even if some such explanation as has just been suggested were possible, it does not appear to be the true one. The value of 3·3 kiloms. per second given by Professor MILNE for an arc of 110° depends solely on the Argentine earthquake, and, as shown by the times tabulated above, an even higher rate might have been adopted. The values for 60° and 80° also are lower than might have been adopted if the time of commencement was referred to, while the rate for 20° , though lower than that given by the Turkestan earthquake, may represent closely the average rate for that distance.

In interpreting the data, however, it is necessary to remember the circumstances in which they were obtained. All the data available as yet are from observatories situated in Europe, and consequently we have not observations of the same earthquake at varying distances from the origin, but observations of different earthquakes whose origins were at various distances from the group of observatories at which they were recorded.

Now the waves of the third phase, whatever the nature of the molecular movement to which they are due, travel along the surface as distinct undulations with a motion, to use Professor MILNE's simile,* "not unlike the swell upon an ocean." Such being the case, it is not improbable that their rate of propagation may be dependent on their size, as in the case of sea waves; and this is the more to be expected if, as seems probable, their propagation is partly gravitational.

If this be the case, the instruments would only be affected by earthquakes originating at very great distances if they were of very great magnitude and capable of setting up the largest waves, which would not only travel furthest, but at the greatest speed. In the case of earthquakes originating at more moderate distances, a certain proportion would be of lesser magnitude, setting up surface waves of lesser size, and travelling at lesser velocities, by which the average of the apparent rates of propagation would be reduced. Close to the origin, moreover, we come into the region where earthquakes are sensible, and the very low rates of propagation recorded in some cases would further lower the average.

The interpretation which I put on the records is, therefore, that the third phase corresponds to the arrival of a form of wave motion which is propagated round the surface and not through the interior of the earth; that the rate of propagation in the case of each individual earthquake is practically constant; and that the true and apparent velocities of propagation are everywhere the same, but that the rate of propagation varies in the case of different earthquakes, being dependent in some way on the size of the waves set up by it. In the case of the greatest earthquakes, which are recorded at distances of 60° and over, this rate of propagation appears to be practically always about 2·9 kiloms. per second for the principal and largest waves,

* 'Seismol. Jour. Japan,' vol. 3, 1894, p. 89.

and may rise to over 4.0 kiloms. per second for the long low waves which outrun the principal ones.

The conclusion drawn from the records is greatly strengthened by the fact that, in the case of the great earthquake of 1897, the only one where the rate of propagation has been carefully determined within the seismic area as well as at a distance, it was found that the rate of propagation of the sensible shock, from the origin to distances up to 15° of arc, was practically the same as the rate of propagation of the waves of the third phase to a distance of 65° of arc. The actual difference as calculated is but 0.1 kilom. per second, or about one-thirtieth of the value, a difference which is well within the inevitable limits of error of the observations.

The nature of these waves has yet to be elucidated. The elastic surface waves investigated by Lord RAYLEIGH should travel, in material of the nature of the rocks with which we are acquainted, at a rate of about 0.9 of the rate of propagation of a distortional plane wave in an infinite solid. This for continuous rock of the nature of that which forms the crust of the earth is about 2.6 kiloms. per second, so that if we take the rate of propagation of the greatest surface waves at 2.9 kiloms. per second, the excess is just about what the defect should be.

The form of the molecular movement in the waves investigated by Lord RAYLEIGH, does not seem to be consonant with that recorded in the neighbourhood of the origin. At great distances it may be in closer accord, but apart from this, the rate of propagation of the purely elastic surface waves is not a function of either their length or amplitude, while that of the great surface undulations of an earthquake appears to be a function of one or both of these. This is intelligible if, as was suggested by Lord KELVIN,* the propagation of these waves is accelerated by gravity, and the fact that the rate of propagation seems to be in some way a function of their size is a support to the suggestion.

§ 8. There remain now for notice only those cases where the record has commenced earlier than the time at which the condensational waves, set up by the earthquake to which the record is attributed, would be expected to emerge. In all, seven such cases are included in the records noticed above, and are tabulated below.

Earthquake No.	Arc degrees.	Time of		Interval. Minutes.	Locality.
		Origin.	Record.		
7	41.0	17 ^h 36.0 ^m	17 ^h 37.0 ^m	+ 1.0	Ischia.
7	41.0	15 28.0	15 15.2	- 12.8	"
7	42.4	15 28.0	15 15.0	- 13.0	Catania.
4	72.7	8 7.0	8 7.5	+ 0.5	Nicolaiew.
6	74.2	0 9.4	0 17.0	+ 7.6	"
3	85.2	10 31.0	10 30.0	- 1.0	Shide.
2	155.2	20 50.0	21 0	+ 10.0	Tokio.

* 'Seismol. Jour. Japan,' vol. 3, 1894, p. 87.

Of these the two records of the earlier of the two Turkestan earthquakes of 15th August, 1897, being 13 minutes in advance of the time of origin, may very probably be attributed to some local shock. Three of the others are practically simultaneous with the origin, and one, omitting the Tokio record of the Argentine earthquake, about $7\frac{1}{2}$ minutes later than the origin. That is to say, the record begins from 5 to 15 minutes before the arrival of the condensational waves.

It is very difficult to decide whether these early commencements of the record have any real connection with the earthquakes they appear to refer to, or are due to other, possibly local, disturbances which happened to coincide approximately with the greater earthquake.

On the one hand the number of cases in which there is an early commencement of the record seems too great for the connection to be fortuitous. Excluding the second Turkestan shock, where the record began at Ischia and Catania about 13 minutes before the earthquake, and the disturbance may well be attributed to some other cause, we have no less than five out of ten distinct shocks, in which there is a commencement of the record in advance of the disturbance of what I have called first phase.

On the other hand there is the want of accordance in the times, and the fact that the early commencement was in each case only found at a single station; as these are about evenly divided between the light and heavy pendula, there is no guide as to the nature of the disturbance.

If due to the principal shock and not to local disturbances, these early commencements of the record can hardly be attributed to any form of wave motion set up by, and at the same time as, the earthquake. They would, in this case, have to be attributed to premonitory disturbances of a nature very different to that of the main shock, for, though unfelt in the neighbourhood of the origin, the initial energy of the disturbance would have to be great enough to affect instruments at distances ranging from one ninth to one quarter of the circumference of the earth.

On the whole, then, it seems more natural to attribute these early commencements, which show no concordance in their times as compared with each other, to local disturbances, or at any rate to some cause other than the earthquake with which they are approximately coincident. A possible exception to this is the Tokio record of the Argentine earthquake; this, as suggested above, may be due to the earlier emergence of condensational waves which have traversed the central core of the earth, as compared with those which have not penetrated so deep and, though traversing a shorter course, have done so at a lower rate of propagation.

The results obtained in the preceding investigations may be summarized as follows:—

1. The complete record of a distant earthquake shows three principal phases of increase of displacement followed by decrease, the phases being marked by a more

or less well defined change in the character as well as the amount of the displacement. Of these the third phase is the most readily and constantly recorded, the second less so, and the first is the phase most frequently absent.

2. The disturbance of the first and second phases being recorded by heavy pendula, possessing great inertia, with greater constancy and concordance than by light horizontal pendula specially designed to detect surface tilting, we may conclude that the motion is principally of a to-and-fro nature, and that the records are due to the inertia of the pendula, rather than to a tilting of the surface. This conclusion has been come to by previous writers in the case of particular shocks.

3. The times of arrival of the first two phases, when plotted, form a curve of increase of apparent velocity with distance, consistent with the hypothesis that they represent the times of arrival of elastic waves propagated through the earth at rates which increase with the depth below the surface.

4. The increase of rate of propagation with depth appears to be a constant function of the depth, at any rate as far as the greatest depth reached by the waves which emerge at a distance of 90° of arc from the origin. Beyond this depth, which may be put at about 0.45 of the radius, there are some indications of a rapid increase in the rate of propagation.

5. The time curves drawn through the times of commencement of the first and second phases, if continued to the origin, give initial rates of propagation in tolerably close agreement with the probable initial rates of propagation of condensational and distortional waves in continuous rock.

6. We may consequently accept the conclusions, that the first phase represents the arrival of condensational waves, and the second phase of the distortional waves, each of which have travelled along brachistochronic paths through the earth.

7. The disturbance of the third phase differs from that of the first, or second, phase in that the light pendula with photographic registration are even more sensitive to it than the heavy pendula whose freedom of movement is trammelled by the friction of their mechanical record. From this we may conclude, that the record is due not to inertia, but to a tilting of the instrument as a whole; a conclusion which is borne out by the nature of the record in those instruments which trace the displacements on a surface moving with sufficient rapidity to give an open record. This is the phase of the long surface undulations, resembling the swell of the ocean, whose character has been recognised and acknowledged since 1894.

8. The apparent rate of propagation of the waves of this phase shows no sign of varying with the distance from the origin, but is constant at all distances, or at most subject to a very slight and slow change. From this it may be concluded that they are propagated as surface undulations and that, in their case, the true and apparent velocities are everywhere identical.

9. The rate of propagation is not, however, constant in the case of all earthquakes, but the waves set up by the greatest earthquakes travel at a higher speed than

those set up by lesser ones ; from this it may be concluded that the rate of propagation is, in some way not yet worked out, a function of the size of the wave.

10. The rate of propagation of the waves of this phase is, in the case of great earthquakes, higher than that which has been calculated for purely elastic surface waves, and from this, and from the fact that their rate of propagation seems to be a function of their size, it is probable that their propagation is, at least in part, gravitational.

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IV. *Impact with a Liquid Surface studied by the aid of Instantaneous Photography.*
Paper II.

By A. M. WORTHINGTON, M.A., F.R.S., and R. S. COLE, M.A.

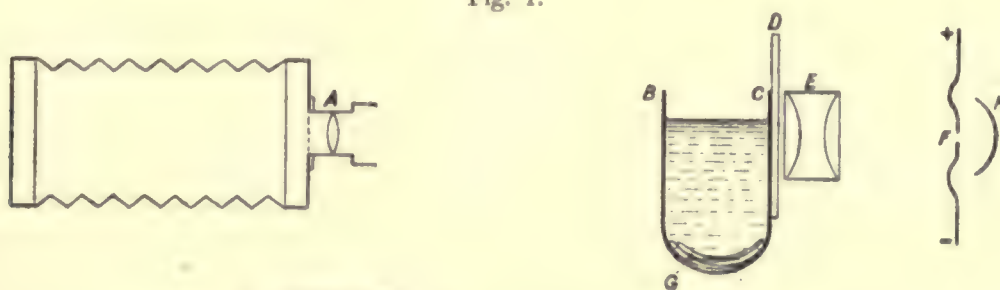
Received March 21,—Read May 4, 1899.

[PLATES 2-3.*]

IN a previous paper ('Philosophical Transactions,' A, 1897, vol. 189, p. 137) we have drawn attention to the fact that the disturbance set up in a liquid by the impact of a rough sphere falling into it, differs in a very remarkable manner from that which follows the entry of a smooth sphere. In the present paper we describe further experiments, made with the object of ascertaining the reason of this difference, and give the conclusions reached.

It appeared desirable, in the first place, to take instantaneous photographs of the disturbed liquid below the water-line. These were easily obtained by letting the splash take place in an approximately parallel-sided thin glass vessel (an inverted clock-shade) illuminated from behind. The liquid surface when undisturbed was about level with the middle of the camera-lens, which was focussed for the sphere when under water. The general arrangement of the optical apparatus will be sufficiently understood from the accompanying cut (fig. 1). The method of timing the illumination was that already described (*loc. cit.*).

Fig. 1.



- A, camera lens.
- BC, vessel with liquid.
- D, plate of finely roughened glass.
- E, condenser taken from an optical lantern.
- F, spark-gap at centre of curvature of concave mirror.
- M, concave silvered watch-glass.
- G, copper gauze to break the fall of the sphere.

* The photographic illustrations accompanying the manuscript of this paper are silver prints mounted on ten sheets, which are referred to as "sheets" in the text. Certain figures from these sheets have been selected for collotype reproduction, and are given on Plates 2 and 3. Others are given in the text. When a figure is referred to which is not reproduced either by photography or by a cut in the text, the No. of the figure is enclosed in [].

The first series of these photographs (see Sheet 1, from which a selection is reproduced on Plate 2) is, for the sake of clearness, called Series X., so as to keep the numbering continuous with the previous paper. The photographs show what is going on below the surface of the liquid while the phenomena of Series VIII. of the previous paper are visible above the surface.* The sphere was a rough marble, freshly sand-papered on each occasion.

The photographs 1 and [2] show the sphere gradually entering the surface; above it is the inverted image of the part that has entered, formed by internal reflection on the liquid surface. Higher up still (in fig. 1) and not quite in the same vertical line (on account of a slight optical displacement due to the front of the vessel not having been set quite perpendicular to the line of sight) is seen the top of the sphere. This, however, is out of focus, for the camera was focussed on the part under water, which is optically brought forward.

In figs. [3, 4] and 5 it will be observed that the liquid already leaves the sphere along a tangent, and from this point onward the sphere is followed by a bag or pocket of air of gradually increasing depth. The wall of this pocket is not quite smooth, and the summit of the sphere, as seen through it, is always somewhat distorted. The sharp angle made with this wall by the oppositely sloping wall of the image tells in each figure the position of the surface, and in several figures we see the lobed lip of the crater that has been already photographed from above in Series VIII. The present photographs show the exact height of this. It will be observed that the depth of the crater or pocket below the surface is far greater than the photographs of Series VIII. gave any reason to suspect, also that the upper part of the sphere is not wetted at all.†

We can find no trace of any reflecting layer of air between the lower part of the sphere and the water, and have no reason to doubt that the lower part is thoroughly wetted up to the place at which the liquid is seen to leave it. As the sphere descends the position of the circular line of contact rises on the sphere and the liquid does not always leave it along a tangent. The ripple-marks conspicuously visible in fig. 9, and in many of the later figures, are indications of the flow of the liquid along the walls of the cylinder of air. The long cylindrical hollow that is thus formed is not a configuration of stable equilibrium, and, if we may leave momentum out of account, its law of spontaneous segmentation will be the same as for a liquid column of the

* This series of photographs, with the exception of the last two, was taken in June, 1896, and was exhibited at the soirée of the Royal Society in June, 1897.

† The present photographs, taken in conjunction with those of Series VIII. of Paper I., bring out a point which had escaped us. For it is now evident that the hollow below the surface in such figures as 8, 9, and 10 of Series VIII. is far too deep and capacious to be filled by the small amount of liquid raised above the general level at the edge of the water, and can, therefore, only be accounted for by a *rise of the general level*, extending to a very considerable distance from the splash. We showed that this phenomenon accompanied the entry of a smooth sphere; we now see it to be even more marked with a rough one.

same dimensions—in air. Thus the cylinder finally divides into two portions, one of which follows in the wake of the sphere as an attached bubble (figs. 16 and 17), while the other rapidly fills up, apparently, or at any rate in part, by the pouring in of liquid round the rim of the basin. The convergence of this inward flow corresponds to an increasing velocity as the axis is approached, and results in the very rapid upward spirt of the jet that is so well shown in Series VIII. of the previous paper.

Our opinion that the basin does fill up by a motion of this kind is based upon the evidence of the photographs of Series XII., which will be explained shortly. Meanwhile it is convenient to point out that Series XI. (here shown by drawings) gives the under-water phenomena corresponding to Series IX. of the previous paper. In this the sphere (still *rough*) is let fall from a greater height, 50 centims., and the crater thrown up closes and forms a bubble which subsequently opens again and makes

Series XI.

Fig. 1.



Fig. 2.

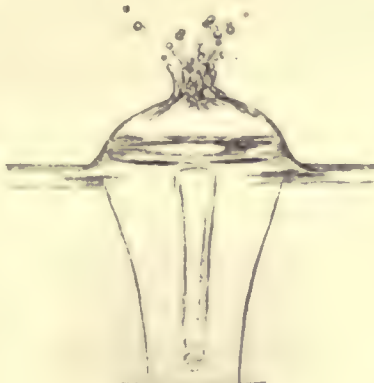


Fig. 3.

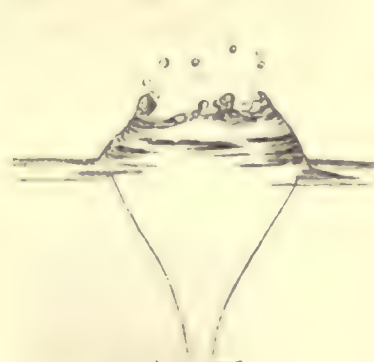


Fig. 4.

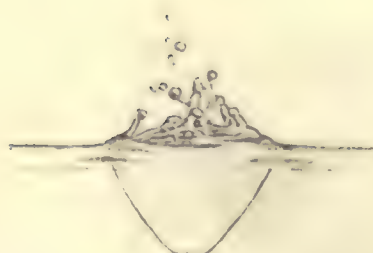
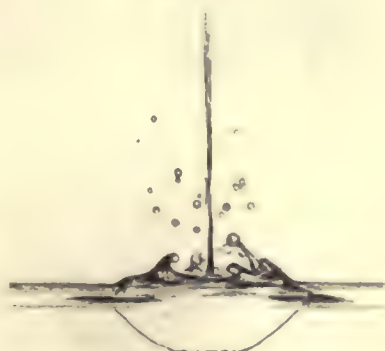


Fig. 5.



way for the emergent jet (*cf.* Series II., figs. 16, 17, and 1A, and Series III., fig. 18, of the earlier paper).

In order to obtain, if possible, some information as to the actual motion of the liquid, a variety of experiments was made with coloured bands and floating bodies, and finally we hit upon the method of letting the sphere fall into dilute sulphuric acid between two electrodes (the bared extremities of two insulated vertical copper wires), from each of which there ascended slowly a vertical stream of very minute bubbles liberated by electrolysis. The velocity of ascent of these bubbles, though it was not always quite slow enough to avoid eddying motion, was so slow (about $1\frac{1}{2}$ centims. per second) that the gravitative displacement of any one bubble during a splash is practically negligible, and the line of bubbles may be therefore taken as a line of marked liquid whose displacement can thus be studied, for the bubbles are so small that it may, we think, be safely assumed that they did not in any way interfere with the motion of the neighbouring liquid. On account of this minuteness the stream of bubbles is not always easy to see in the photographs, and in printing from the negatives long exposure in bright sunshine is necessary.

It will be observed that whereas in fig. 1 of Series XII. (here reproduced) each stream is delivered from the top of the electrode; in figs. 2 and 3 the stream has been swept off the electrode, especially on the left-hand side where the electrode is

Series XII.

Fig. 1.



Fig. 2.



Fig. 3.



Fig. 5.



Fig. 6.



nearer the sphere. Fig. 5 shows that the division of the air column is accompanied by the formation of an annular vortex. Fig. 6 [7, 8, and 9] show the filling up of the crater. The vertical lines of bubbles recover their original positions; but at the top, where the lateral displacement has been greatest, it will be observed, especially in fig. 6, that the stream of bubbles turns over inwards, and it is on this that we rely as proving that in part, at any rate, the hollow fills up by the pouring in of liquid down the sides. There are unmistakable indications of this same curling over in the negative of fig. [8] when the jet has begun; but the stream of bubbles is so faintly visible that it would disappear in any reproduction.

The next step in the investigation was to examine in more minute detail the splash of a *smooth* sphere. For this purpose we procured a number of very hard highly polished steel bearing balls of three sizes,* viz. :—

- (1) $\frac{6}{8}$ inch (= 19.0 millims.) in diameter.
- (2) $\frac{5}{8}$ „ (= 15.9 „) „
- (3) $\frac{4}{8}$ „ (= 12.7 „) „

Several of each size were subsequently coated with an electrolytic deposit of nickel, which took a still higher polish.

In the year 1897 several hundred splashes were observed with these spheres. Previous observations, as recorded in Series IV., V., and VI. of the earlier paper, had shown that when a well-polished sphere enters with a not very great velocity, the liquid rises over it in a thin sheath, covering it completely before it is entirely below the level of the surface, and that such a sphere consequently takes down no air whatever into the liquid; also that the motion of the liquid is different, from the earliest moments of contact, from that set up by the entry of a rough sphere. We had, however, noticed that with a much-increased height of fall the smooth sphere took down air and behaved like a rough one.

It appeared possible to us that there was some critical velocity which might mark the change very sharply, and accordingly our first observations were directed to the examination of this point. It was not necessary for this to use any instantaneous illumination; the magnetically-controlled “catapult” release was still employed for letting the spheres fall, but the observations were conducted in the full light of the laboratory. The results of some hundreds of observations may be summarised as follows :—

With any one sphere always carefully polished in the same way just before letting it fall, a height of fall is soon reached at which the splash ceases to be “completely airless” or smooth, but is followed by the rise of bubbles, at first a shower of very

* We afterwards, as will be seen, employed spheres, 25.7 millims. in diameter, of polished serpentine, and may here state at once that we have not found that the size of the sphere has, within the limits mentioned, any noticeable influence on the course of the splash.

small and inconspicuous bubbles, afterwards when the height is increased, of large and very visible bubbles.

Thus the transition from "smooth" to "rough" is gradual. But the equilibrium of the splash, if we may use the phrase, is very unstable and very much depends on the condition of the surface of the sphere when dropped in.

Thus a polished steel sphere 15.9 millims. in diameter was found to give an airless splash when falling into water from a height of 132.5 centims. ; at 137.5 centims. there was much air taken down. This observation at 137.5 centims. was repeated three times, Observer C doing the polishing. Then Observer W polished, and the splash was first *nearly* airless, then *quite* airless. Then, by persevering in the rubbing, the height of fall was gradually raised to 162.5 centims., and a perfectly airless splash was secured ; and even at 172.5 centims. the record was "very little air indeed."

Again, a polished marble sphere 2.57 centims. in diameter falling into water from a height of 112 centims. was found to take "much air" when rubbed with clean handkerchief, A, and "none at all, or only very little," when rubbed with clean handkerchief, B. This result was confirmed four times with B, and five with A. These handkerchiefs were subsequently examined under the microscope, but were found to be extremely similar, and the cause of the difference remained for the time beyond conjecture.

On another occasion, of two similar nickel-plated steel spheres, each 19 millims. in diameter, and each treated in exactly the same way, falling 22 centims. into paraffin oil, one would always take down much air and the other little or none, and again microscopic examination showed only a very slight difference in the surfaces.

Influence of the Nature of the Liquid.

The nature of the liquid employed has a great influence in determining whether at a given height the splash shall be "rough" or "smooth."

Thus with paraffin oil the maximum height that could be reached with an airless splash with highly polished nickel-plated spheres, well rubbed on a selvyt cloth, was found to be only 24.7 centims., but with water a fall of 160 centims. could be reached. Whenever water was used as the liquid it was contained in a deep glass bowl, kept brim-full and running over by means of an india-rubber supply pipe from the main, so that the surface was kept perfectly clean. The Devonport water is drawn from a granite country, and is very soft and pure.

We shall revert later to the manner in which the physical constants of the liquid come into play.

Influence of Temperature.

We then found that if the polished sphere was heated in boiling water, quickly rubbed dry, and let fall while it was still hot, a very marked difference was produced.

With the polished sphere hot, the height of fall can be much increased before the splash becomes "rough." Thus, with paraffin oil, the height with a nickelled sphere rose from 22.2 centims. to 29.3 centims., and with water from 157 centims. to 234 centims.

Influence of a Flame held near the Liquid, and traversed by the Sphere in its Fall.

It then occurred to us to let the sphere drop through a flame held near the liquid, and the result was very remarkable. With paraffin oil (and the sphere hot) the airless height now rose from 29.3 centims. to 45.3 centims., and with water and a cold sphere, it rose from 157 centims. to over 258 centims., which was the greatest height that the laboratory would permit. Either the luminous flame of a bat's wing burner or the flame of a Bunsen burner held nearly horizontal produces the effect, provided the flame is held near enough to the surface of the liquid, and it is a very striking experiment to let the polished sphere fall several times from a height which gives a large volume of bubbles rising with much noise to the surface, and then to let it fall through the flame, and to observe the complete change in the phenomenon.

Electrification.

It seemed to us extremely probable that we had here to deal with an electrical phenomenon, for a flame would certainly discharge completely any electrified sphere passing through it, and it appeared reasonable to suppose that the sphere became electrified by friction when falling through the air. Experiments were therefore made to test this supposition. Holding the flame high above the surface should diminish the effect, for the sphere would become again electrified in the remainder of its fall. Experiment abundantly confirmed this view. Thus, with the maximum height of fall available (258 centims.), the flame was still quite effective at 68 centims. above the surface of flowing water, but quite ineffective at 113.5 centims.

Nevertheless, other tests failed to confirm this theory of electrification. If the difference is due to electrification, we argued, then it ought to become very conspicuous when the sphere is deliberately electrified. Accordingly, a long series of experiments was made, in which the sphere soon after its release came into contact with a flexible wire brush connected to a Wimshurst machine, and thus was electrified positively or negatively at pleasure. A height of fall was then chosen for which the splash was either just airless or just not airless when the sphere was unelectrified, so that the influence of electrification in changing the character of the splash either way could be observed.

The results of these observations were curiously discordant,* and though it is

* The probable reason will be mentioned later.

proverbially difficult to prove a negative, the conclusion was finally forced upon us that this electrification, whether positive or negative, had no certain or direct influence. We also tried the effect of holding a charged ebonite rod near the splash, but with negative results.

One test we were able to make which appears to us to be crucial. If the flame acts by diselectrifying the sphere, then the same result should follow from letting the sphere touch in its fall an earth-connected brush near the water, but such contact had no observable effect whatever, and we therefore came to the conclusion that the action of the flame was not an electrical discharging action at all.

In this connection also may be mentioned two other facts: (1) That the flame had no observable effect on a roughened sphere; and (2) that we could not detect any accumulation of electricity when we let the sphere fall time after time through a tube connected to an electroscope, to which tube the sphere could give up its whole charge by touching a wire brush in the interior.

Photographs of the Transition from "Smooth" to "Rough."

Having found that the splash passed by gradual transition from "smooth" to "rough" as the height of fall of a polished sphere was increased, we decided to obtain a photographic record of the process. Series XIII., Sheet 3, of which a selection is here reproduced on Plate 2, shows a perfectly smooth splash produced by a highly polished sphere of serpentine, just over 1 inch (2.57 centims.) in diameter, falling into water from a height of between 14 and 15 centims.

The earlier figures of this series show how extremely thin is the enveloping sheath in its early stages. In fig. 1 it is almost best seen by its reflected image in the undisturbed surface. A nearly horizontal row of minute drops may be seen in figs. [2] and 3. As we shall see later, the place of origin of any one of these is to be found very approximately by drawing a tangent to the sphere through the drop in question in the plane containing the axis, for unless the velocity of the sphere is very materially altered after the moment of separation, the drop will remain on the tangent along which it was projected. The "lug" at either side in figs. [2] and 3 is probably not really the continuous jet it seems to be, but merely the fore-shortened edge of a ring of separate droplets, as is more apparent in figs. [4] and 5. Where the horizontal equator of the sphere is passed, the film will thicken by convergence, and the number of segmentations will diminish accordingly, the drops becoming larger and fewer. It will be noticed that in each of the figs. 5 and 6, a vertical tangent to the sphere marks the limit of the larger drops in the air above.

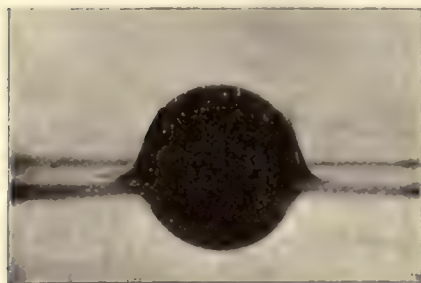
Fig. 8 shows by means of bubbles that the displacement of the liquid corresponds approximately to stream-line flow in a perfect fluid.

Series XIV., Sheet 4, of which fig. 1 is given on p. 183, shows the effect of increasing

the height of fall to 50 centims. It will be observed that the minute jets* projected from the edge of the film are now much higher, while in Series XV. (see fig. 2 here reproduced), in which the height of fall was raised to 75 centims., we see that the

Series XIV.

Fig. 1.



Series XV.

Fig. 2.



film has left the sphere at an earlier stage, and has more nearly the configuration observable in a rough splash. In Series XVI., of which figs. 1, 2, and 3 are reproduced in Plate 3, the height of fall was 100 centims., and the change was still more marked. No air is taken down by this splash.

In order to avoid the necessity of a somewhat inconveniently great height of fall, which would have been imposed by the further use of water as the liquid, we employed Alexandra oil for watching below the surface the beginning of the process by which the sphere takes down air in its wake. Thus Series XVII., Sheet 5, here reproduced in the text, shows the splash of a polished nickelled-steel sphere

Series XVII.

Fig. 1.



Fig. 2.



* The photographs (unfortunately not the reproductions here given) both of this and of our previous paper illustrate incidentally the great rapidity with which fine jets undergo division into drops, which, however, as Lord RAYLEIGH has explained ('Roy. Soc. Proc.' vol. 29, 1879, p. 85, on the Capillary Phenomena of Jets), need cause no surprise, since the time of complete segmentation will vary inversely as the $3/2$ power of the diameter—if viscosity does not hinder.

Series XVII.

Fig. 3.



Fig. 4.



19 millims. in diameter falling 30 centims. into Alexandra oil, a height at which ordinary observation in continuous light had shown that a little air was already taken down. In Series XVIII. the height was 40 centims., and in Series XIX. it was 50 centims.

Series XVIII.

Fig. 1.



Fig. 2.



Fig. 3.

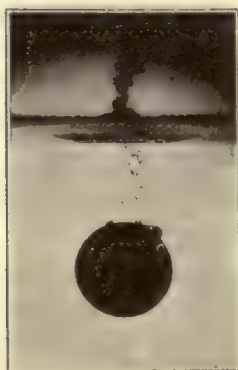
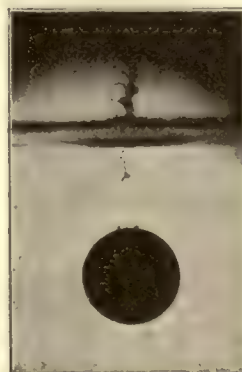


Fig. 4.



Series XIX.

Fig. 1.



Fig. 2.



Fig. 3.



Fig. 4.



Fig. 5.



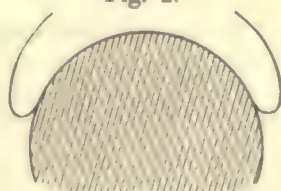
Fig. 6.



In every case there is a quasi-stream-line convergence of flow in the rear of the sphere which was not observable in the rough splash ; this sweeps together the bases of the jets in the crater above the surface, and the entrapping of air seems to depend on the depth to which the sphere has descended when the convergence is completed, and cannot now be attributed, as in the "rough splash," to the spontaneous segmentation of a cylindrical cavity too long to be in stable equilibrium.

It should be mentioned that the bubble is liable to detach itself from the sphere, either wholly or in part, before any considerable depth is reached ; thus, in figs. 2 to 6 of Series XIX., careful examination of the photographs with a lens shows that the liquid is beginning to pass along the surface of the sphere between it and the air in the manner indicated (with exaggeration) in the accompanying cut (fig. 2).

Fig. 2.



The minute but deep corrugations on the surface of the air-bubble in fig. 6 are probably indications of rapid turbulent motion at the interface.

We may here recall to the recollection of the reader that a remarkable feature of the sheath enveloping a smooth sphere, entering with low velocity, was the strongly accentuated radial ribs and flutings (*cf.* Series XXVI., figs. 1 and 3, p. 196), which are specially well seen in the figs. 3, 4, 5, and 9 of Series VI. of Paper I. The present photographs, taken, as they are, with the light behind the object, do not bring these out very well, but traces of them may be detected with a lens in the original photographs, though not in the present reproductions, on the under surface of the liquid to the left of the sphere in figs. 1 and 2 of Series XVII., and in figs. 1 and 2 of Series XVIII., on the right side of the sphere in fig. 1 of Series XIV., and again in fig. 4 of Series XVI.; and it must not be forgotten that they are probably always present. Of this fluting we shall be able presently to give a pretty complete account.

General Explanation of the Phenomena.

The explanation which seems to give the key to the whole phenomenon was suggested (1) partly by the observation of AITKEN that dust does not settle on an object hotter than the air, (2) partly by the observation of QUINCKE that a film of extremely small thickness spreads with great rapidity by molecular action over a polished surface, *e.g.*, of glass or mica when this is touched by a liquid, and (3) partly by our own observation that, at any rate in the neighbourhood of the surface, a flow once set up along any channel is comparatively persistent and determines the motion that is to follow. As illustrations of this we may cite the regular disposition of jets round the rim of the crater thrown up by an entering drop, which persists for a comparatively long time, and is apparently due to the spontaneous segmentation of the annular rim at a very early stage; or, again, the very strongly salient ribs of flow just alluded to (see Series VI. of our first paper), each of which seems to correspond to one of the jets.

This general explanation is as follows:—

When a sphere, either rough or smooth, first strikes the liquid, there is an impulsive pressure between the two, and the column of liquid lying vertically below the elementary area of first contact is compressed. For very rapid displacements the liquid on account of its viscosity behaves like a solid. In the case of a solid rod we know that the head would be somewhat flattened out by a similar blow, and a wave of compression would travel down it; to this flattening or broadening out of the head of the column corresponds the great outward radial velocity, tangential to the surface, initiated in the liquid, of which we have abundant evidence in many of the photographs.

Into this outward flowing sheath the sphere descends, and since each successive

zone of surface which enters is more nearly parallel to the direction of motion of the sphere, the displacement of liquid is most rapid at the lowest point, from the neighbourhood of which fresh liquid is supplied to flow along the surface. Whether the rising sheath shall leave the surface of the sphere or shall follow it depends upon the efficiency of the adhesion to the sphere. If the sphere is smooth, the molecular forces of cohesion will guide the nearest layers of the advancing edge of the sheath, and will thus cause the initial flow to be along the surface of the sphere.

To pull any portion of the advancing liquid out of its rectilineal path the sphere must have rigidity. If the advancing liquid meets loosely attached particles, *e.g.*, of dust, these will constitute places of departure from the surface of the sphere; the dust will be swept away by the momentum of the liquid which, being no longer in contact with the sphere, perseveres in its rectilineal motion. If the dust particles are few and far between, the cohesion of the neighbouring liquid will bring back the deserting parts, but if the places of departure are many, then the momentum of the deserters will prevail. Thus at every instant there is a struggle between the momentum of the advancing edge of the sheath and the cohesion of the sphere; the greater the height of fall the greater will be the momentum of the rising liquid, and the less likely is the cohesion to prevail, and the presence or absence of dust particles may determine the issue of the struggle.

Roughness of the surface will be equally efficient in causing the liquid to leave the sphere. For the momentum will readily carry the liquid past the mouth of any cavities (see fig. 3), into which it can only enter with a very sharp curvature of its

Fig. 3.



path. It is to be observed that the surface tension of the air-liquid surface of the sheath will act at all times in favour of the cohesion of the sphere, and even if the film has left the sphere the surface tension will tend to make it close in again, but we should not be right in attributing much importance to this capillary pressure which, with finite curvatures, is a force of a lower order of magnitude*

* This point may be made clearer by a numerical statement of the case. The particles of the liquid sheath on the shoulders of the sphere (itself *descending*) in figs. 5 and 6 of Series XIII., Plate 3, must be describing paths whose centres of curvature lie on the side of the sphere, and on every element of the film there must be an inwardly directed force. (We speak of the film as a whole, and ignore any minute vortical motion.) With a sphere of 1 centim. radius, and water as the liquid, the surface-tensional pressure would be about 0.075 gramme per sq. centim., which is quite insignificant as compared with the

than the cohesion, and, as later photographs will clearly show, is incompetent to produce the effects observed.

In order to test this general explanation further experiments were made.

Experiments on the Influence of Dust.

In the first place, to test the influence of dust, the experiment was made of deliberately dusting the surface of the sphere. For this purpose highly polished nickelled spheres, of the three sizes mentioned on p. 179, were held in a pair of crucible tongs by an electrified person standing on an insulating stool, and by him presented to any dusty object that stood or could be brought within reach. The particles of dust soon settled on the electrified sphere, which was then carefully placed on the dropping ring with the dusty side lowest. The liquid used was Alexandra oil, and the height of fall was 31.7 centims., at which each of these spheres when not dusted gave still a quite airless splash. When dusted an enormous bubble of air was carried down by each. Although the spheres when laid on the dropping ring must have completely lost their electrical charge, yet it seemed worth while to go through the same electrifying process without dusting them. The result showed that no change was produced. In order to see how far the influence of dust would go, the height of fall was now reduced, and it was found that with sphere (1) a fall of 17.1 centims. gave a perfectly rough splash when the surface was visibly dimmed with fine dust, and with sphere (3) a fall of 16.7 centims. availed. If the surface was only slightly dusty, then at these heights the splash remained "smooth."

It then occurred to us to try the effect of partial or local dusting, for we had already found by experimenting with a marked sphere that the method of dropping did not impart any appreciable rotation to the sphere, which reached the liquid in the attitude with which it started from the dropping ring. Accordingly, after dusting the sphere in the manner already described, the dust was carefully rubbed away from all but certain parts whose position was recorded. The experiments were very successful, and the results are shown in Series XX. The liquid used was water, and the sphere was of polished serpentine, 25.7 millims. in diameter, falling 14 centims. (*cf.* Series XIII., Plate 3).

In fig. 1 of Series XX. (see Plate 3) the sphere was dusted on the *right-hand* atmospheric pressure on the outside, which would be about 1,033 grams per sq. centim. If the actual centripetal pull per unit area is less than this, then the hydrostatic pressure, even at the inner side of the film, will still be positive. If a greater pull than this is required, the hydrostatic pressure near the inner side of the film must be negative, and the liquid there will be in a state of true tension. Experiments which we have conducted *in vacuo*, and which will be described later, show that when this true tension is reached the liquid is *liable* to separate from the solid and to "cavitate," and the phenomenon of a smooth splash then ceases with the guiding influence of the sphere. Thus the limiting value of the cohesion which can be reached in practice is probably about 1,038 grams per sq. centim.

side and a "sound of splash" was recorded. On the left side there is no disturbance of the "smooth splash"; on the right is a "pocket" of air such as was obtained by accident in Series VI., fig. 4, of the earlier paper (here reproduced as fig. 2A for convenience of reference and to help the reader to interpret correctly the first and second figures of the present series). The point of departure at which the liquid left the sphere is well marked, and a tangent from this point passes through the outermost conspicuous droplets that must have been projected from it.

In fig. 2 the sphere was dusted *at the top and on the right-hand side, but not much more than halfway down*, and the configuration corresponds entirely to the facts. Here again a tangent from the well marked drops on the right-hand side leads very nearly to the place of departure from the surface of the sphere.

In fig. 3 on this page the record is that the sphere was dusty at the top only. It is to be expected that dusting at the top will not make *much* difference in the flow of the already converging liquid. Comparison with fig. 7 of Series XIII., Plate 3 shows, however, that a slight effect has been produced.

Series XX.

Fig. 3.

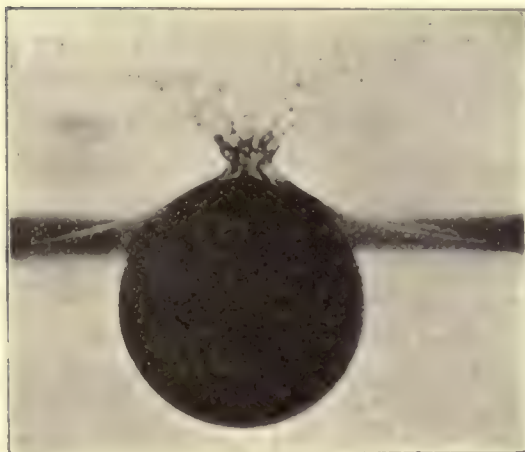
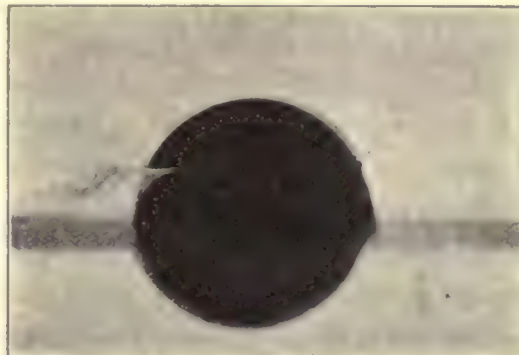


Fig. 4.



In fig. 4 the sphere was dusted at the bottom only. The appearance on the left-hand side seems to show that the liquid has, after leaving the sphere, again been brought within reach. This recovery at an early stage is explained by reference to photographs of Series X. of the splash of a rough sphere, which show that even the rough sphere is soon wetted for some distance up the sides, as we may imagine by the gradual passage of the sphere into the divergently flowing cone of liquid which surrounds the lower part. When the liquid again touches a polished part the film will be again guided up it in the manner already explained. In figs. 5 and 6 (shown in drawings on page 190) the sphere was out of focus through the slipping out of place of the rod which held the releasing gear—a fault which was not discovered till

after the photographs had been developed. In each case the sphere was dusted on the right-hand side *along a narrow vertical strip*. In No. 5 the tangent from the highest drops on the right again leads accurately to the place of departure of the liquid. In fig. 6 the pocket of air has apparently been swept up the surface of the sphere, perhaps by the converging flow already noted.

Series XX.

Fig. 5.

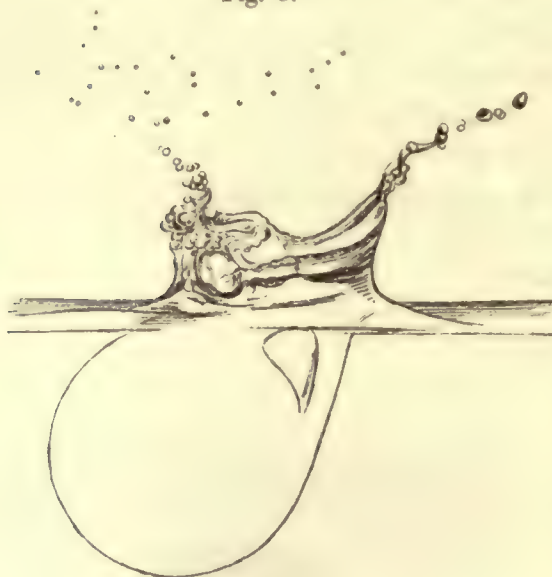


Fig. 6.



We observe that in figs. 1 and 2 (same Series XX., Plate 3) the continuous film or shell of liquid no longer reaches the outermost droplets that once have been at its edge. It must evidently have been pulled in by its own surface tension, which of course will cease to exercise any inward pull on a drop that has once separated.

The influence of dust, thus incontestably proved, seems to afford a satisfactory explanation of—

- (1) The effect of a flame.
- (2) The effect of heating.
- (3) The variable and uncertain effects of electrification.

For (1) we may suppose that the flame burns off minute particles of dust; (2) we know from AITKEN'S experiments that dust from the atmosphere will not settle on a surface hotter than the air; (3) an electrified sphere descending through the air would attract dust to its surface unless it happened, as well might happen, that the air round about it, with its contained dust, had become itself similarly charged through the working of the electrical machine.

At the same time we cannot claim that our explanation of the influence of a flame is more than a conjecture. For we found that it was only when the brightly

polished metal spheres were dusted nearly to dimness that the splash was invariably altered, but when we let such a visibly dusty sphere drop through a flame and then caught it in a conical wire cage, the dust was not found to be burned away or appreciably altered, *nor in this case was the splash altered by passage through the flame.* This shows that there is a kind of dust which cannot be removed by a flame, and it is only a conjecture, however probable, that there is a kind which can. We have sought to bring the matter to a crucial test by dropping the sphere through filtered and, presumably, dust-free air contained in a long wide iron pipe whose lower end was just submerged in water; but though the result of many such trials seemed to show that the splash near the critical height was more often "smooth" in the dust-free air than in ordinary air, there were too many exceptions for the matter to be put beyond doubt.

In further confirmation of our view that the leading clue to the explanation of the motion is the struggle between the adhesion of the rigid sphere and the tangential momentum of the liquid, we may cite the following points:—

A *liquid* sphere (see Series I., II., III. of Paper I.) makes a "rough" splash, and the photographs obtained show that the lower part of the in-falling drop is swept away by the tangential flow, while the upper part is still undistorted.

Here we have cohesion but no rigidity. And we have found that the "rough" splash is obtained by any process which gives a non-rigid surface to the sphere. Thus the splash made by a marble freshly roughened by sand-papering, or by grinding between two files and let fall from the very small height of 7.5 centims., can be practically controlled by attending to the condition of the surface. If the surface is quite dry and still covered with the fine powder resulting from the process of roughening, the splash is "rough," and a great bubble of air is taken down. But if this coat of powder, which has neither cohesion nor shearing strength, be removed by rubbing, the splash (under this low velocity) is "smooth." Again, a marble freshly sand-papered and covered with the resulting powder, if let fall from 12 or 15 centims., gives a rough splash. The same marble picked out of the liquid and very quickly dropped in again from the same height, will give again a rough splash. Here the liquid film is thick and "shearable." But if the same sphere be allowed to drain or be lightly wiped, the splash will be smooth. Here we may conjecture that enough fluid is left to fill up the interstices, but that the coat is not thick enough to shear easily. If, however, the sphere be thoroughly dried the splash becomes "rough" again. This gives us the explanation of the facts already recorded in respect of the splash of a wet sphere (Series VII. of Paper I.). This splash was always irregular; the liquid drifted to one side where it would shear, while it disappeared from the other or became there too thin to shear, though sufficient to fill up crevices.

Explanation of the Flutings.

The fact thus established experimentally, that the surface of a smooth sphere must be rigid if the film is to envelope it closely, suggests what seems a satisfactory explanation of the flutings. For it suggests that, even while the film is exceedingly thin, the flow is of the kind demanded by POISEUILLE, in which the liquid next to the solid has no motion relative to the solid, while the velocity farther away increases with the distance from the surface. Since the sphere is descending while the film is rising, there must be a strong viscous shear in the liquid impeding its rise. If by any fortuitous oscillation a radial rib arises, this will be a channel in which the liquid, being farther from the surface, will be less affected by the viscous drag; it will therefore be a channel of more rapid flow and diminished pressure, into which, therefore, the neighbouring liquid will be drawn from either side. Thus a rib once formed is in stable equilibrium, and will correspond to a jet at the edge of the rim. This explains the persistence of the ribs when once established, and we may attribute their regular distribution to the fact that they first originate in the spontaneous segmentation of the annular rim at the edge of the advancing sheath. This explanation receives unexpected confirmation in the appearance of the lop-sided splashes of Series XX., in which we see, firstly, that the flutings are absent from that part of the sheath which has left the sphere, and, secondly, we see how much higher in every case the continuous film has risen in that part which has left the sphere than in the part which has clung to it, and has been hindered by the viscous drag. Especially is this the case in fig. 3, Series XXVI. (see p. 196), where the liquid was pure glycerine. The effect of the viscous drag is, in fact, most marked in the most viscous liquid.

Influence of the Constants of the Liquid.

Finally, in confirmation of the general argument, we have the fact that with a liquid of small density and surface tension, such as Alexandra oil, a much smaller velocity of impact with a highly polished sphere is required to give "rough" splash than with water, a liquid of greater density and surface tension, the reason being without doubt that the tangential velocity due to the impact is greater with the less dense liquid, as, indeed, is proved to be the case by the greater height to which the surrounding sheath is thrown up, and the smaller the surface tension the less will be the abatement of velocity on account of work done in extending the surface.

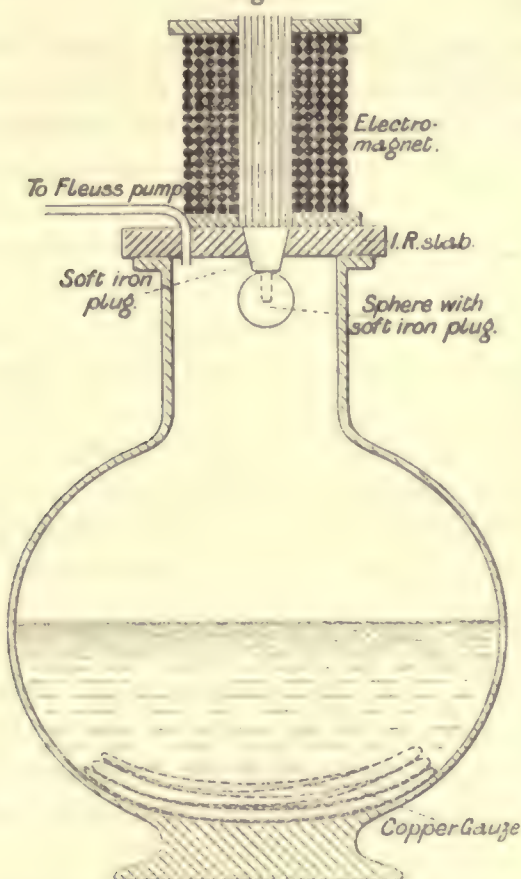
[*Added January 11, 1900.*—The constants of the Alexandra oil employed in the experiments were as follows: *Specific Gravity*, 0.840; *Surface Tension*, 2.89 grams per metre (= surface tension of water \times 0.383); *viscosity* = viscosity of water at the same temperature \times 2.607. Experiments shortly to be described show that the addition to 51 vols. of water of as much as 6 vols. of glycerine, which must have largely increased the viscosity, produced little difference in the splash, except in

making the ribs more noticeable, and we therefore conclude that within these limits the viscosity does not play an important part in determining the main course of the phenomenon.]

Experiments in vacuo.

It remained to examine what part was played by the air in the whole transaction. This could only be settled by removing the air. We accordingly made provision for obtaining, by instantaneous illumination, observations of splashes *in vacuo*. The method was simple enough, since, happily, very exact timing was not necessary. For eye observations a large, strong "bolt-head" was employed, and a 1-inch thick slab of india-rubber closed it air-tight (see fig. 4). This slab was pierced at one side by a glass tube leading to a Fleuss pump, and centrally by a short thick conical piece of soft iron, which served as the prolongation of the core of a straight electro-magnet which could be laid on the top. A pad of folded, fine woven, copper wire-gauze* prevented the bottom of the vessel being broken by the impact.

Fig. 4.



The nickelled and polished steel spheres were at first employed, but these retained so much of their magnetism that the timing was very uncertain, and they were after-

* We have found a pad of this material very convenient and efficient in all our experiments.

wards discarded for spheres of marble and serpentine, into which a deep hole was drilled, and into this a soft iron plug inserted. After each splash the air had to be re-admitted, the electro-magnet removed, and the vessel opened and the sphere fished out by means of a long, clean, bar-magnet.

The exhaustion was always pushed to within 2 or 3 millims. of a perfect vacuum, the vapour only of the liquid being left. The first observations were made in broad daylight, with a highly polished nickel sphere (size 1), dusted and undusted, and also with a rough marble sphere, 25.4 millims. in diameter. The observations were alternated by others, in which all conditions were the same except that the air was not removed. In no case could any difference be observed with the naked eye. Thus the polished sphere took down no air when clean, made a large bubble, or sometimes a "rough" column, when dusted, and the rough sphere always went in "rough" and made a high column. The depth of fall was 19.5 centims.

When spark-illumination was used with the small rough sphere, the figures [6], 8, and 10, and the upper part of [7] of the rough-sphere splash of Series X., Plate 2, were obtained repeatedly.

Even with the Fleuss pump, which works very quickly, it was a work of some minutes to exhaust this large bulb to within 1 or 2 millims. of a vacuum. During this time the electro-magnet had to be kept running, and became hot, and the time of de-magnetisation thus depended, more than was desirable, on the previous history of the magnetisation.

In order not to waste time and photographic plates, we exchanged this large vessel for a tall "gas jar" of smaller volume, through which the image was, indeed, a good deal distorted, but this does not much diminish the value of the record. We used both water and Alexandra oil as the liquids, and give, on Sheets 7 and 8, a few of the photographs thus obtained.

Inspection of these photographs shows only two points of difference of importance between the splash *in vacuo* and the splash in air.

The first of these is the significant point that it is not so easy to secure a quite smooth splash *in vacuo* for the reason, as we may confidently surmise, that the liquid, being supersaturated, is liable to burst into ebullition at the surface of the entering solid, where probably, as already explained in the note on p. 196, the velocities set up correspond to a true negative pressure or tension, under which the liquid will readily rupture and break away from the solid surface if any cavity is formed. Indeed, it should be mentioned that until the vessel had been many times exhausted of air, bubbles were very liable to form spontaneously in the liquid and rise from the bottom (boiling by bumping).

Fig. 1 of Series XXI., Plate 2, shows, for purposes of comparison, a smooth splash in air (height of fall, 14 centims.), while fig. 2, and also [3] and [4] (not here reproduced), show the near approach attained *in vacuo*, and the development of bubbles. Fig. [5] (not here given) shows a splash *in vacuo*, in which at an earlier

stage the ensheathing film was almost complete. This photograph is practically identical with fig. 6, Series XIII., Plate 3.

Passing now to the "rough" splash, we have, in fig. 1, of Series XXII., Sheet 8 (see Plate 3), a "rough" splash in air; in fig. 2, the same *in vacuo*; in fig. [3], a later stage *in vacuo*. The liquid in each case was water, and the height of fall, 13.5 centims. Figs. [4] and [5] show the collapse of the vacuous column formed behind a rough sphere falling into Alexandra oil. In each of these last there is an appearance of folding at the surface, which was not observable when air was present. And we see the beginning of the same kind of thing on the left-hand side in fig. 2.

This difference, which is probably due to negative pressures induced by vortical motion near the interface, appears, however, to be quite a secondary matter, and does not prevent us from asserting that the presence of the air has no material influence on the early course of the splash, except, as already explained, in respect of the extent to which its pressure serves to relieve the liquid from a cohesive tension under which it would cavitate.

Experiments with a Viscid Liquid.

It appeared probable that experiments made with water thickened by successive additions of glycerine would throw light on the part played by viscosity in the transaction. With a mixture consisting of water 51 vols., glycerine 2 vols., no change of any kind was perceptible in the splashes observed. When the glycerine was increased to 6 vols. in 51 of water, the disturbance set up was still extremely similar, as will be seen by comparing the figures of Sheet 9, which represent the splash of a smooth serpentine sphere in the glycerine mixture at the heights specified, with the corresponding figures in the case of water, Sheet 4, Series XIV. and XVI. The only noticeable difference is the rather greater salience of the ribs in some of the glycerine figures, and the greater reluctance in the jets to segment into droplets.

We then experimented with pure glycerine. Series XXVI. of Sheet 10, reproduced in part on page 196, gives the splash in pure glycerine of the same polished serpentine sphere, 25.7 centims. in diameter, falling 75 centims. In all cases the radial ribs are seen in the negatives of the photographs to be very pronounced. Even at so early a stage as fig. 1 the fluting is well developed. The two photographs taken of stage 3 had each of them an isolated jet, probably owing to the fact that when working with so sticky a liquid it was difficult to avoid contaminating the cloth on which the sphere was each time re-polished after washing in water, with the result that the sphere behaved as if locally rough. The relatively great length of this jet brings out very well the part played by the viscous drag in hindering the flow of that portion of the liquid sheath which has remained in contact with the sphere. In the last figure No. 4, of this series the droplets just visible in the centre, below the level of the general surface, correspond to those of figs. 6 and 7 of Series XIII. at a much higher

Series XXVI.

Fig. 1.

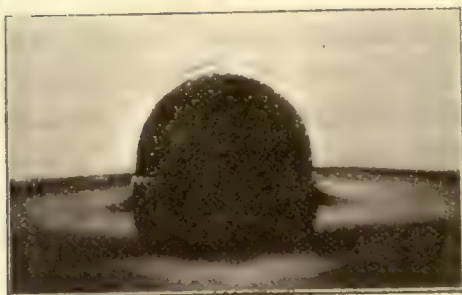


Fig. 3.

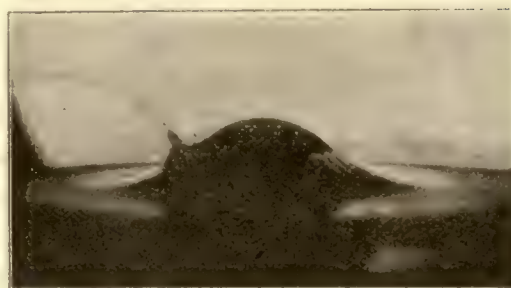
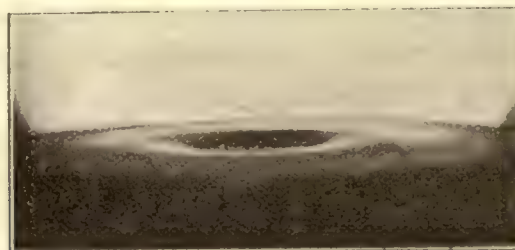


Fig. 4.



Series XXVII.

Fig. 1.

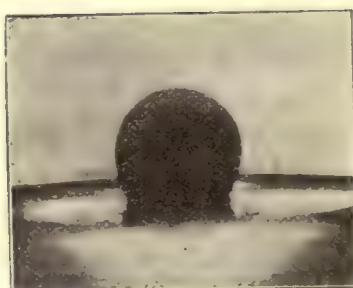


Fig. 2.

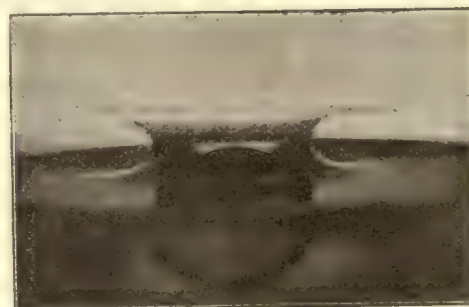
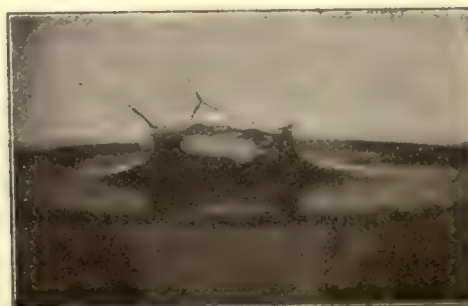


Fig. 3.



level, their presence in the lower position being again due to the slower convergence of the liquid sheath.

When we came to experiment with *rough* spheres falling 75 centims. into pure glycerine, the first photographs obtained were figs. 2 and 3 of Series XXVII., here given, which correspond very closely with figs. 2 and 3 of Series IX. of the former paper, obtained when a similar sphere fell 60 centims. into water. But when we adjusted the timing sphere so as to obtain earlier stages, expecting such a figure as No. 1 (which was actually taken from a water splash with 14 centims. fall), we obtained instead such figures as 1, 2, and 3 of Series XXVIII., in which the fall

Series XXVIII.

Fig. 1.



Fig. 2.

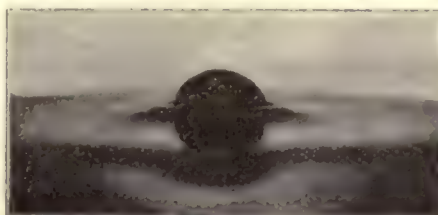


Fig. 3.



Fig. 4.

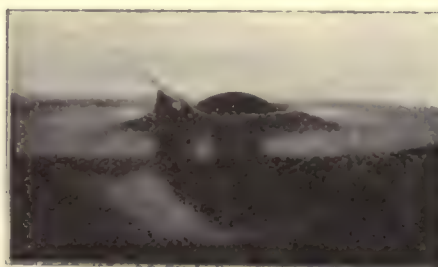
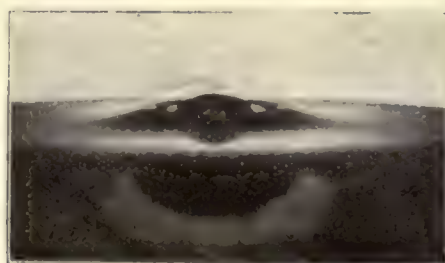


Fig. 5.

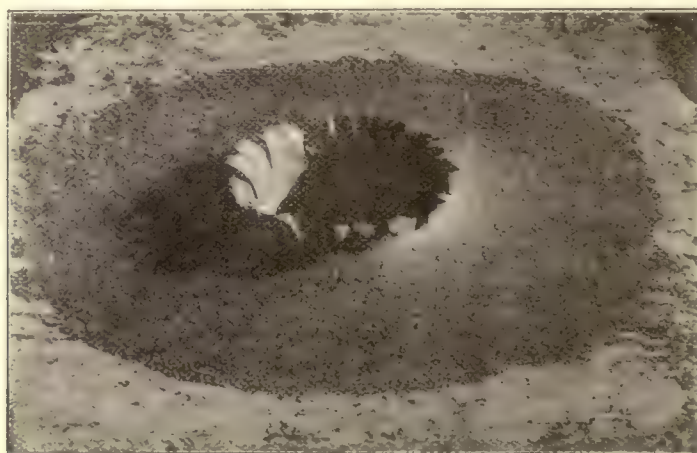


was the same, viz., 75 centims. Being convinced that the extreme fringe of the crater in fig. 2, Series XXVII., could only have been projected at a very early stage, we made repeated experiments to discover the cause of the contradiction, and found

that such figures as 2, and 3, and 4 of Series XXVII. were only obtained after the glycerine had stood long enough for the exposed surface to absorb a film of water from the air. Thus, if the glycerine was freshly stirred, Series XXVIII. was invariably obtained, but if it stood for twelve hours exposed to the air of the laboratory the splash was that of Series XXVII. We found that the gain of weight was about 0.01 gramme per sq. centim. of exposed surface in twenty-four hours, so that the water absorbed in twelve hours would, if it remained on the surface, form a layer about $\frac{1}{20}$ of a millim. thick. Using a fall of 204 centims., we found by naked eye observation that the water absorbed in six hours did not suffice to change the splash, while that absorbed in twelve hours always sufficed. These observations throw a striking light on the determining importance of the initial motion. It should be mentioned that in Series XXVII. the temperature of the glycerine was 15° C., and in Series XXVIII. was 12° C., except in the last figure, when the fall was 100 centims. and the temperature 22°.

Further experiments with viscous liquids are very desirable, as they may enable us to pass by gradual transition to phenomena which at first sight may appear to be far removed. For if any one will compare with fig. 2 of Series XXVII., the accompanying photograph of the permanent record left of the splash which a steel projectile makes on entering a hard steel armour plate on the entering side, he will find it difficult to resist the belief that the plate has behaved like a liquid. Yet even the

Fig. 5.



whole kinetic energy at disposal in such an impact would not suffice to raise the projectile itself through more than a few hundred degrees Fahrenheit, still less to melt at the same instant any appreciable quantity of metal, and we are therefore driven to the conclusion that under the enormous pressure due to the impact the physical properties of the material of the plate have been so far altered as to change entirely the conditions of liquefaction,

Series XII.

Fig. 1.

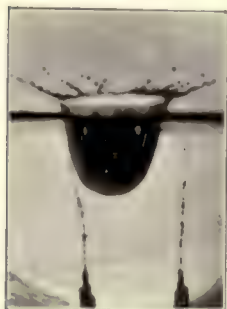


Fig. 2.



Fig. 3.



Fig. 5.

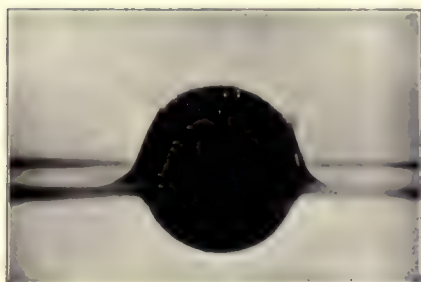


Fig. 6.



Series XIV.

Fig. 1.



Series XV.

Fig. 2.



Series XVII.

Fig. 1.

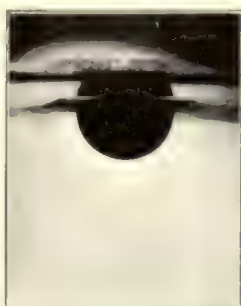


Fig. 2.



Fig. 3.

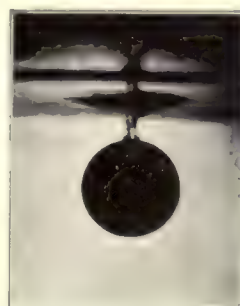
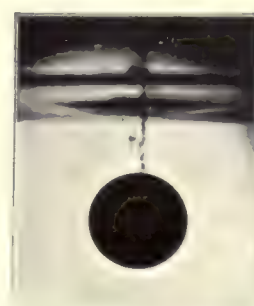


Fig. 4.



Series XVIII.

Fig. 1.



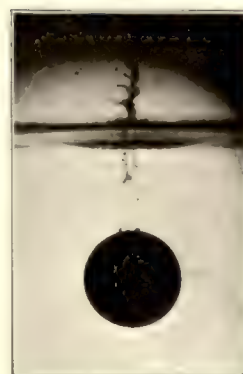
Fig. 2.



Fig. 3.



Fig. 4.



Series XIX.

Fig. 1.

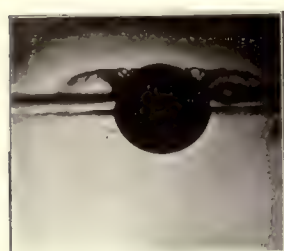


Fig. 2.



Fig. 3.

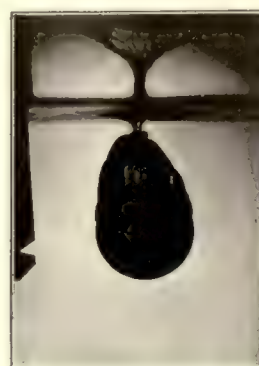


Fig. 4.



Fig. 5.



Fig. 6.



Series XX.

Fig. 3.

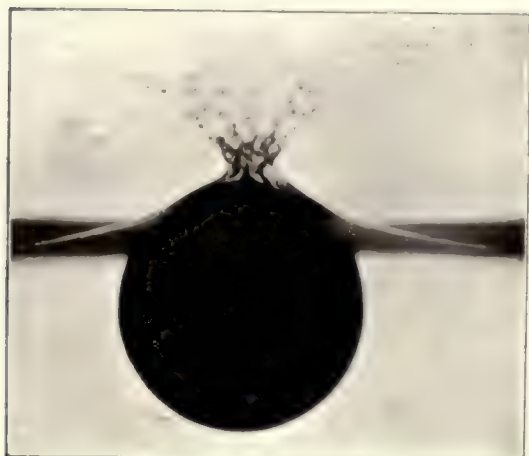
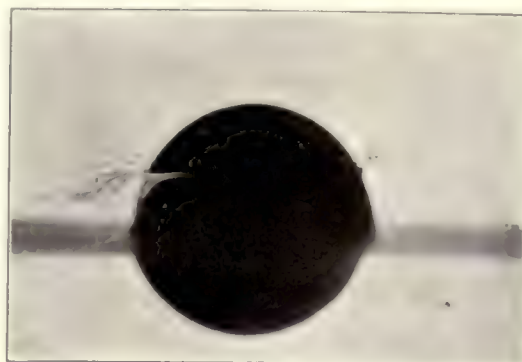


Fig. 4.



Series XXVI.

Fig. 1.

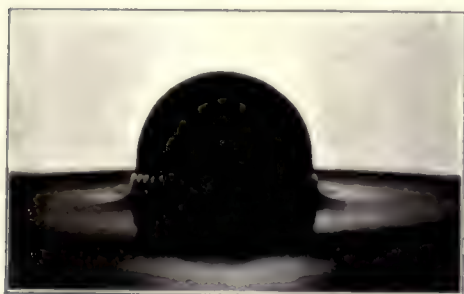
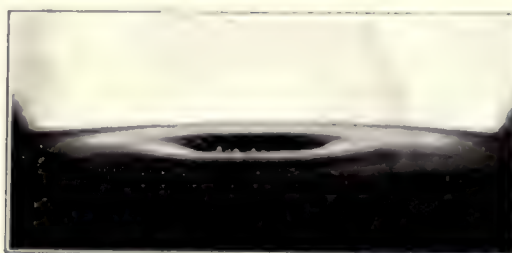


Fig. 3.



Fig. 4.



Series XXVII.

Fig. 1.

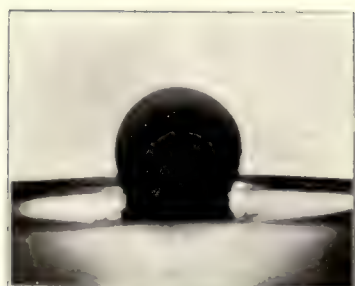
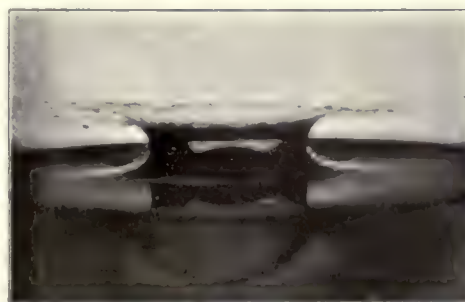
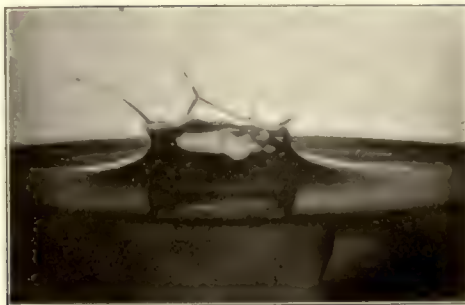


Fig. 2.



Series XXVII.

Fig. 3.



Series XXVIII.

Fig. 1.



Fig. 2.

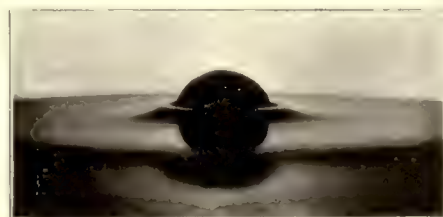


Fig. 3.



Fig. 4.



Fig. 5.

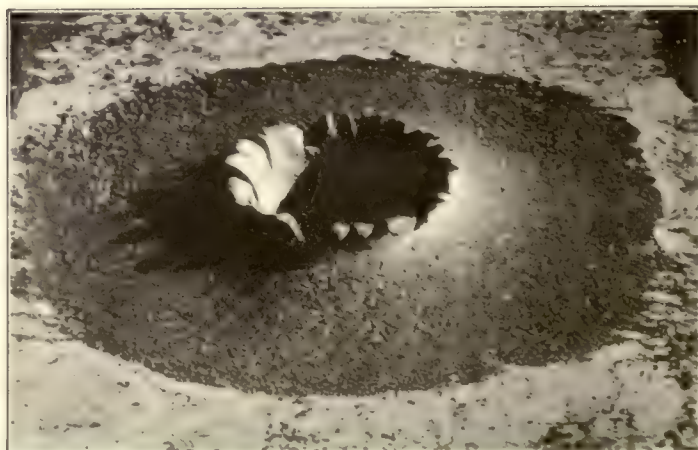
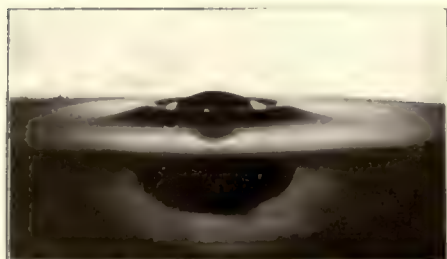


Fig. 5.

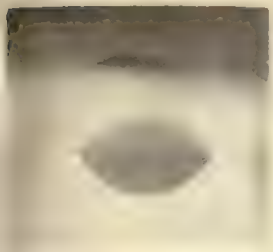


Such a conclusion, if established, would have practical importance in many mechanical processes. It could probably be tested by a microscopic examination* of specimens of the metal of the plate taken from the immediate neighbourhood of the "splash," and it is interesting to recall in this connection the argument of Professor POYNTING in his paper on the Change of State: Solid—Liquid ('Phil. Mag.,' July, 1881), that the rate of exchange of molecules across any surface will increase with the pressure.

* Since this was written Sir WM. ROBERTS-AUSTEN has most kindly examined for us specimens of the metal taken from the "burr" of such an armour-plate splash, and reports that he finds no traces of liquefaction having occurred. It therefore appears that, even in this extremely rapid deformation, we may have to attribute the plasticity and quasi-fluidity of the metal to the same slip along surfaces of cleavage within the crystals of the material, which Professor EWING and Mr. ROSENHAIN† have shown to take place when the deformation is much more slowly effected.—(Note, October 8, 1899.)

† 'Roy. Soc. Proc.,' May 25, 1899, vol. 65; 'Phil. Trans. R.S.,' Series A, vol. 193, 1899.





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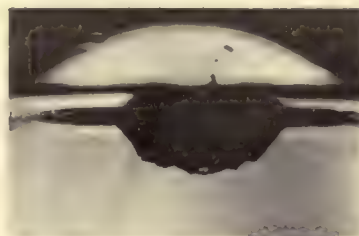
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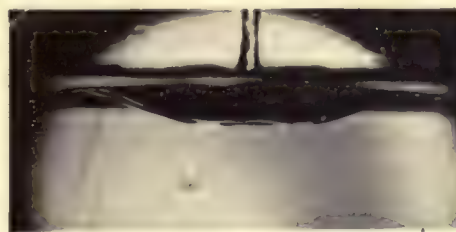
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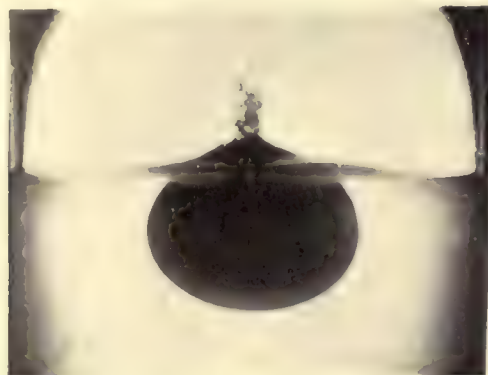
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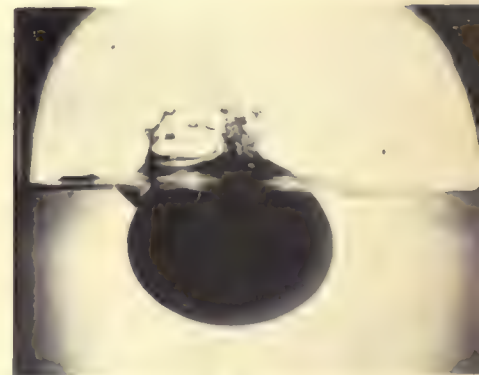
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SERIES X.

SERIES XXI.

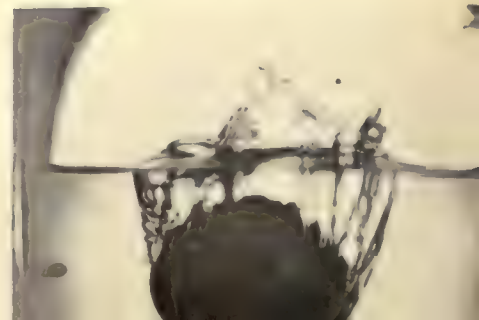
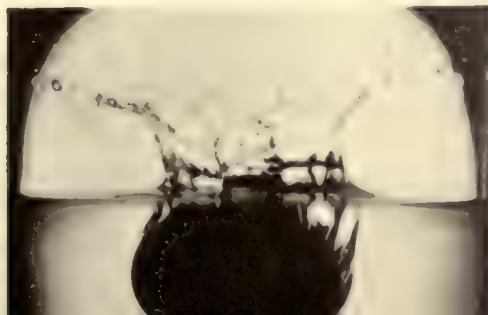


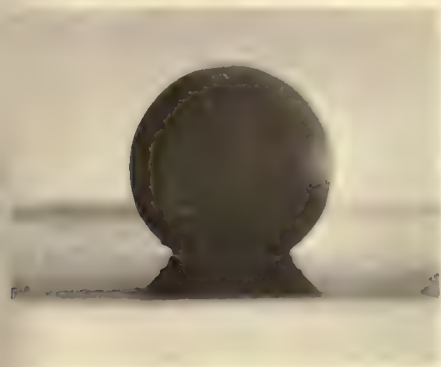
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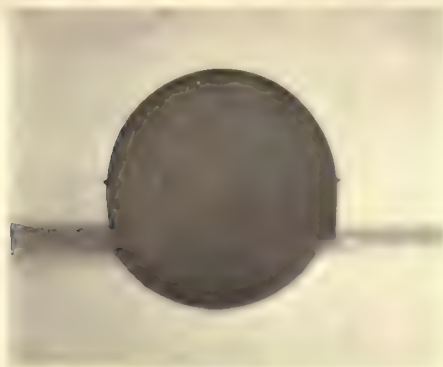
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SERIES XXII.

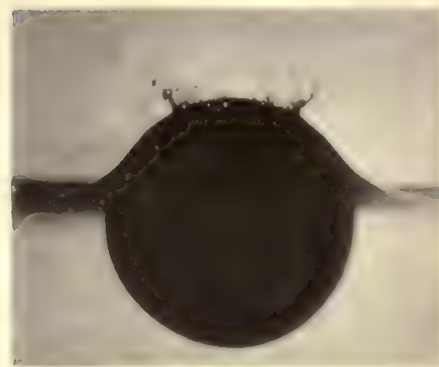




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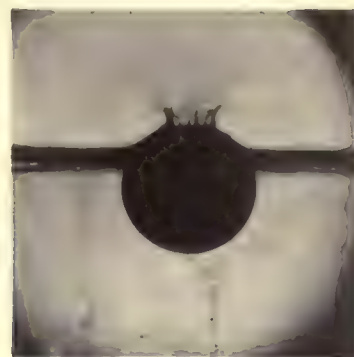
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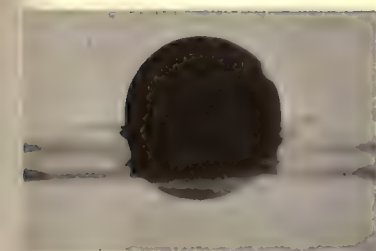


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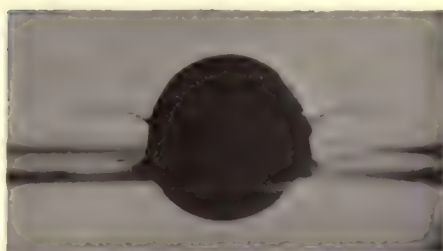


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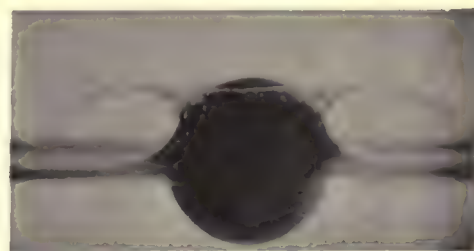
SERIES XVI. (100 cm. fall).



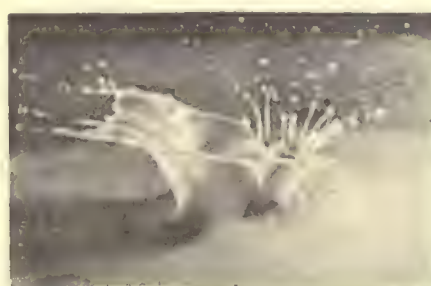
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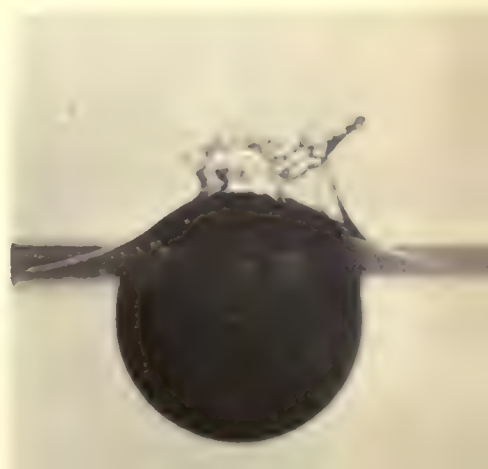


3



2A.

SERIES XX.



V. *Gold-Aluminium Alloys.*By C. T. HEYCOCK, *F.R.S.*, and F. H. NEVILLE, *F.R.S.*

Received October 31,—Read December 7, 1899.

[PLATES 4-5.]

THIS paper is a study of the binary alloys composed of gold and aluminium. The fact that metals in many cases form definite chemical compounds with each other, is becoming increasingly evident as attention is given to the subject. But there are many pairs of metals whose freezing point-curve affords no indication of chemical combination, and which probably do not combine with each other under the conditions of our experiments. It is therefore desirable, in seeking for such compounds, to select a pair of metals which are known to have a peculiar relation to each other. We chose gold and aluminium for several reasons. First, on account of the beautiful purple compound of Sir W. ROBERTS-AUSTEN, and on account of our own experiments ('*Journal Chemical Society*,' vol. 74, 1894), which showed it to be a very stable body in solution. There was also the important point that the alloys of gold and aluminium admit of fairly rapid analysis by the determination of the gold.

In the present paper the freezing point method is combined with a microscopic study of the alloys, and we hope that it will be found that the interpretation of the results is more conclusive than in previous papers of our own and of others in which only the one method or the other was employed.

Section I. describes the methods of experiment.

Section II. contains tables of freezing points, figures of the freezing point-curve, and an account of the curves.

Section III. is devoted to a description of the microscopic appearance of the alloys, and is illustrated by photomicrographs.

SECTION I.

In the experiments on which the freezing point-curve is based, the method of procedure was similar to that described in our paper ('*Phil. Trans.*,' A, vol. 189, p. 25) on the freezing point of copper tin, silver copper, and other alloys.* The freezing point of pure gold was first determined, and then successive roughly weighed amounts of aluminium were added, the freezing point being taken after each addition.

* For the method of determining temperatures, see also our paper ('*Journ. Chem. Soc.*,' 1895, p. 160).

Owing to the rapid oxidation of the aluminium, even when a current of coal gas was led into the crucible, the synthetical method of arriving at the composition of the alloys from the weights of metal added was impracticable. It was therefore necessary, between every two readings of the freezing point, to extract a sample of the alloy for analysis. This was done by sucking out a portion of the thoroughly molten and stirred metal in a pipette of Jena combustion glass. If rapidly performed, this process is practicable, even at the melting point of gold. The samples were thus obtained in the form of rods, or occasionally as tubes, about 4 millims. in diameter. After breaking off the glass these rods could easily be cut up for analysis and for microscopical study. The order of operation was as follows :—

- (1.) A dose of aluminium was added, and the alloy well stirred.
- (2.) The freezing point was determined roughly.
- (3.) The metal was re-melted, stirred, and a sample extracted.
- (4.) The alloy was again re-melted, if necessary, and the freezing point determined accurately.

The cycle was then repeated.

Except when we approached the composition AuAl_2 , each sample extracted was a rod of very uniform composition, so that analyses of the upper and lower portions gave identical results. But at the very high temperatures of extraction needed for alloys near AuAl_2 , the operation had to be conducted very rapidly on account of the softening of the Jena glass, and it was not always possible to obtain solid rods. In such cases the upper and lower portions of the same extract sometimes differed in their composition to the extent of almost 1 per cent. This and other causes, which will be referred to later, made the determination of the curve in the neighbourhood of AuAl_2 a difficult matter.

The analyses were conducted as follows :—A weighed quantity of the alloy, from 2 to 4 grammes, was digested with aqua regia in a covered porcelain dish, until all soluble matter had dissolved. It was then evaporated with excess of hydrochloric acid, diluted and filtered. The residue on the filter paper seldom weighed more than a few milligrams, except when portions of glass adhered to the alloy. This residue was ignited and weighed; it consisted, partly at all events, of graphite. The weight of the residue was subtracted from the weight of the alloy taken for analysis, and the difference regarded as pure alloy. The filtrate containing the chlorides of gold and aluminium was considerably diluted, and the gold precipitated by sulphurous acid gas. The gold was filtered off, ignited and weighed, and the percentage of gold in the pure alloy thence calculated. In the majority of cases we obtained the percentage of aluminium by difference, assuming that the pure alloy contained only gold and aluminium. This procedure was justified for all parts of the curve except those near AuAl_2 , by the test analyses given in square brackets in the tables, in which a complete determination, both of the gold and of the aluminium was made. In these test

cases the aluminium was determined by evaporating the filtrate from the gold in a porcelain dish to remove the sulphurous acid, adding a few drops of methyl-orange and precipitating the aluminium by a very slight excess of ammonia. The liquid was then heated just to boiling and the alumina filtered off on the pump, washed, dried and strongly ignited in a platinum crucible. The gold and aluminium add up to the weight of the pure alloy, except when we are dealing with alloys not far from AuAl_2 . But in the complete analyses of alloys in this region the gold and aluminium usually add up to only a little over 99 per cent. of what we call the pure alloy. It was noticed that in these alloys the residue was always larger than in alloys formed at lower temperatures. We do not feel absolutely certain as to the nature of the missing 1 per cent. It was certainly not due to errors in the estimation of the gold or aluminium, but we are inclined to attribute it to the presence of a considerable amount of carbon in the alloy weighed. In most of these cases the alloy had been exposed for several hours to a temperature of over 1000° in contact with the carbon of the crucible and of the stirrer. Under these circumstances the alloy certainly took up carbon mechanically, and a portion of this carbon, which would be in a very fine state of division, probably disappeared either during the solution of the alloy in aqua regia, or, more probably, during the subsequent ignition of the residue.

In those cases where both the gold and the aluminium were determined, it was easy to ascertain with certainty the atomic percentage.* Curve 4 gives a small number of points near AuAl_2 , which were determined in this way; they are free from any source of error known to us. In all the other points determined in this region the aluminium was arrived at by difference only, and it is not improbable that some of the alloys may have contained quite one atomic per cent. less aluminium than our tables indicate. We have not attempted to correct for this error on the main curve, but we feel quite sure that it is sufficient to account for the summit in Curve 3 lying a little to the right of the formula AuAl_2 .

Near the lower summit of the curve, corresponding to Au_2Al , it will be seen from the tables that it is immaterial whether the composition is arrived at from the percentage of gold alone, or from a complete analysis. We believe that this is true for all alloys containing less than 50 atomic per cents. of aluminium. The aluminium itself was, as analysis shows, very pure, and it, apparently, only takes up carbon and other impurities after a prolonged exposure to a very high temperature.

* For example, take the alloy in which the percentages directly determined were

Au 93.21 per cent., Al 6.86 per cent.

Dividing these numbers by 197.2 and 27.08, the atomic weights of gold and aluminium respectively, we get the formula

Au 0.4727, Al 0.2533.

Hence the atomic percentage of aluminium is

$$\frac{0.2533}{0.4727 + 0.2533} \times 100, \text{ that is, } 34.89.$$

The Curve.

The curves record the freezing points observed during the experiments. The mean composition of the alloy in the crucible is represented in atomic percentages by the figures above each curve, and temperatures are measured vertically in degrees Centigrade, and recorded by the figures below the curves. For the sake of conciseness we shall use the term *atoms* instead of atomic percentages. A statement of the number of atoms present completely determines the composition of the alloy, it being understood that the number of atoms of gold is obtained by subtracting the number of atoms of aluminium from 100.

Let us consider the case when the alloy in the crucible has, taken as a whole, the composition AuAl , that is to say, contains 50 atoms of aluminium. The observed points on a vertical line drawn through 50 give a record of the way in which the alloy cools and solidifies. Above 850° it is wholly liquid, but when the crucible has cooled to this temperature there is an evolution of heat causing the thermometer to remain stationary for a short time, and we observe the upper freezing point. The cooling soon recommences, but more slowly than before, and when the temperature has fallen to 625° there is another halt. After some time, however, the temperature again begins to fall, and soon falls rapidly until about 568° is reached, when an extremely steady temperature is indicated, and the alloy, if it has not done so before, sets to a solid mass. These three points are the freezing points of the alloy. They may, of course, be due to any exothermic changes going on in the crucible, such as the breaking up of the alloy into conjugate liquids or to allotropic changes; but the microscope has satisfied us that in the case of gold-aluminium we have only to do with the separation of solids, in fact, that at each of the three observed points a new substance begins to solidify.

It will be seen that multiple freezing points, although frequent, are not universal; for example, the alloys Au_2Al and AuAl_2 have only one freezing point.

It is important to bear in mind that the diagrams of Curves 2 and 5 give a record of all the freezing points observed, and contain more information than an ordinary equilibrium curve. The first, or upper, freezing points of each alloy do indeed constitute an equilibrium curve, but our lines of second and third freezing points do not, strictly speaking, belong to the equilibrium curve. For example, the second freezing point which we mentioned as occurring at 625° does not represent a state in which a liquid having the composition $\text{Au}_{50}\text{Al}_{50}$ is in equilibrium with solid. For in the solidification of this alloy the liquid part of the matter in our crucible has, ever since the first freezing point at 850° , been getting richer and richer in gold, until when the freezing point at 625° is reached the matter still liquid is of the composition $\text{Au}_{56}\text{Al}_{44}$ or thereabouts. In fact all the freezing points on the horizontal line through G are points of equilibrium between this same liquid and a certain solid. In an equilibrium curve as usually drawn all these freezing points would be represented by the point G. The other lines of second and third freezing points have a similar meaning.

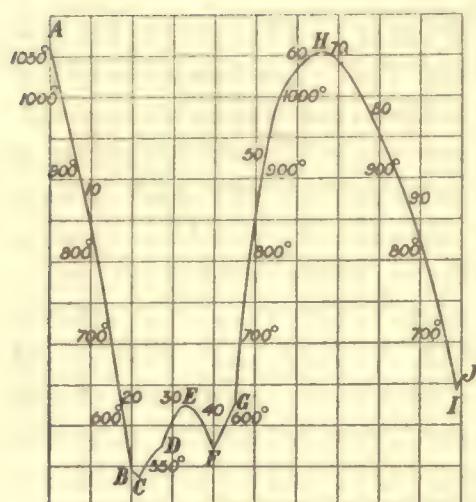
We will now briefly discuss the singularities in the curve.* From A, the freezing point of pure gold, to B, the curve is nearly a straight line. The freezing points of the very dilute solutions are, as usual, very steady temperatures, but as we approach B the upper freezing point is indicated by a slight pause only in the cooling, and lower second freezing points become well marked. These are all at about 545° , and are very steady temperatures. They evidently occur when, after the crystallisation of some gold, the residual liquid has reached a composition of 19 or 20 atoms of aluminium.

From B onwards a new branch of the curve starts which ends in a eutectic point at C, when the alloy contains about 21.5 atoms of aluminium. An alloy of this composition has the low melting point of 525° . This is lower than that of any other mixture of gold and aluminium. We have here the true eutectic of these two metals. The second freezing point at 21 atoms probably belongs to the horizontal line of eutectics through C, which is better marked by other points. There was surfusion at this second freezing point, and therefore it is certain that a new solid now began to form in the crucible. It was noticed that the alloy with 22.3 atoms of aluminium solidified at an extremely constant temperature. This is in harmony with the fact that we are now close to the eutectic angle.

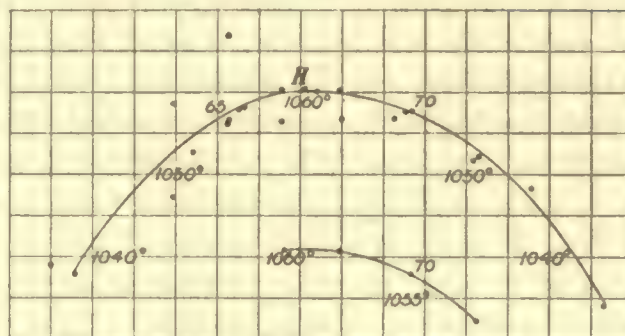
If we pass from C towards D by adding aluminium, the upper freezing point is at first very transient, while the lower one, belonging to the same alloy, is a very steady temperature. But as we approach D, near 28 atoms, the reverse is true. For example, above 26 atoms of aluminium the lower freezing point is lost, and the upper one becomes an extremely steady temperature. Surfusions were noticed at most of the freezing points, both upper and lower, between C and D.

At D there is a singularity in the curve; the freezing points have become very steady temperatures, and, as usual with very steady freezing points, the curve is flat. At a point close to 28 atoms of aluminium a new and rapidly rising branch of the curve begins, the earlier freezing points on it being fugitive. Moreover, through the point of bifurcation the original line of freezing points is continued in a line of second freezing points, which is horizontal for some distance and then descends a little. The points on this line are marked by very steady temperatures like a line of eutectics. From the experimental data for the curve it is difficult to decide whether the summit of the branch CD is to the left or right of the point of bifurcation, or whether there is a short flat to the left of D. But the microscope supplies some reason for thinking that the branch DE cuts the branch CD so that the summit of the latter is a very little to the right of the intersection D, and therefore corresponds to a body that could only be obtained quite pure by surfusion. If we assume that the summit has the formula Au_3Al_2 , it should be at 28.6 atoms of aluminium. The curve of second freezing points starting from D, at first horizontally and gradually sinking, simulates a continuation of the branch CD, but as they

* The rapid depression in the freezing point of gold, due to the presence of small quantities of aluminium, and the great rise in the freezing point as the composition corresponding to the compound AuAl_2 is approached, have been already discovered by Sir William Roberts-Austen.



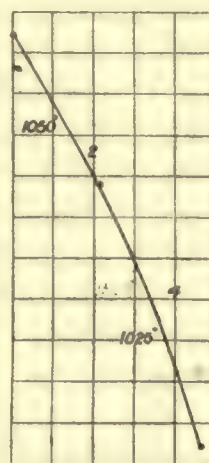
Curve 1.



Curve 3 (upper) and Curve 4 (lower).



Curve 5.



Curve 6.

DESCRIPTION OF THE CURVES.

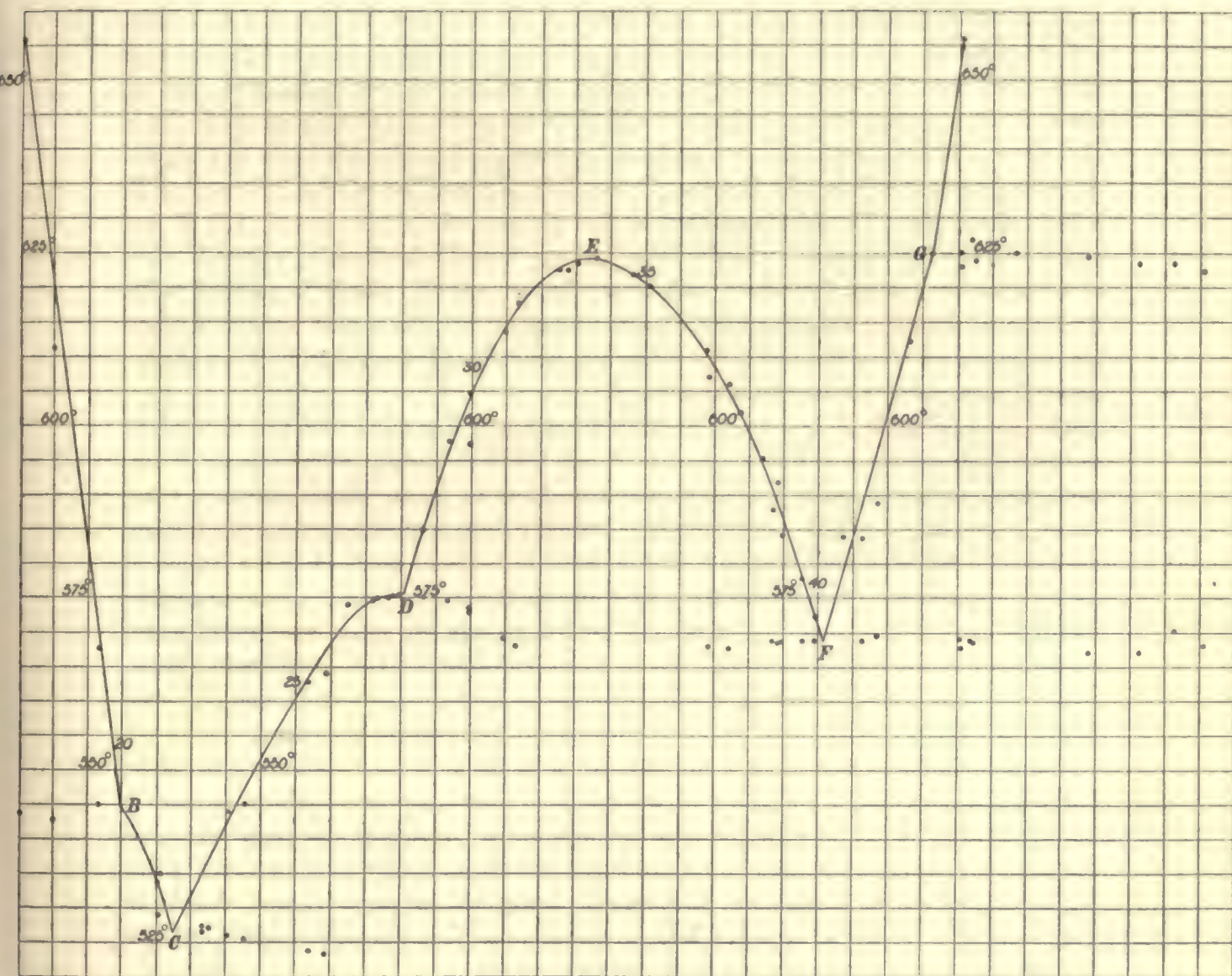
Curve 1 is a diagram on a small scale of the whole freezing point-curve. It is intended especially as a key to the larger figures which give special parts, but it also affords an idea of the relative magnitude of the various branches of the curve.

Curve 2 gives the part of the curve lying between 17 and 44 atoms of aluminium. Experimental points are marked on it by dots, and a continuous line is drawn through the first or upper freezing point of each alloy. This line is what we conceive to be the equilibrium curve.

Curves 3 and 4 give on the same scale the summit of the curve near AuAl_2 , Curve 4 being the most correct. For the points in Curve 4 both the gold and the aluminium were determined; the pyrometer was in good order.

Curve 5 gives the shape of the curve close to the aluminium end, and Curve 6 that close to the gold end.

The numbers placed above the line of the curve are atomic percentages of aluminium, those below the line of the curve are degrees Centigrade. In Curve 5 the numbers plotted are those of the table diminished by 0.7° , to reduce them to our standard value for the freezing point of aluminium, 654.5° .



Curve 2.

were second freezing points and not alternatives to those on the upper line, it is certain that they are not a continuation of CD. We think that, as usual, these second freezing points indicate the moment of solidification of the mother-substance of the alloys between D and E. The composition of this mother-substance would be given by the intersection D, and we should expect it to be an almost pure body. In the case of the alloys near E, the amount of this mother-substance must be very small, the heat produced by its freezing will be small, and therefore thermometer-lag may lower the observed freezing point. This appears a reasonable explanation of the downward curving of the line of second freezing points. The analyses of a number of alloys in this region were conducted with special care, both the gold and the aluminium being determined, and the atomic percentage calculated from their

ratio as well as from the gold alone by difference, the two methods agreeing to within a few tenths of an atomic per cent. It must be remembered that at 27 atoms of aluminium the alloy contains only 5 per cent. by weight of this metal, and that an error of 0.3 per cent. in our analyses would shift the point one atomic per cent. along the curve. It is evident that our analyses are consistent with each other to a higher degree of accuracy than this, but they leave the exact position of the intersection D a little uncertain. The microscope shows that the summit of the branch CD is not exactly at the intersection. On the branch rising from D the freezing points become steadier as we go up the curve, and near the summit E, which is reached with 33.5 atoms, the alloy solidifies wholly at one temperature, like a pure metal. Adding more aluminium after the point E, we have a descending branch ending in a eutectic point F, close to 40 atoms of aluminium.

The eutectic angle F is associated with a horizontal line of second freezing points as usual. Adding more aluminium after F, we follow a steeply rising branch of the curve to G, at which point the alloy contains about 44 atoms of aluminium. Here there is probably a slight angle, another branch rising very steeply from G, while a horizontal row of second freezing points for alloys with more than 44 atoms of aluminium begins. At the freezing points on this horizontal line the halt in cooling was well marked, but not very prolonged, that is to say, no great amount of metal crystallised at the temperature G. These freezing points are not eutectics like those at C and F, nor are they such steady temperatures as those at B, D, and E. We shall find this an important point when we attempt to interpret the curve.

The branch rising from G is steep and the first freezing points are very fugitive; but near the summit H at 66.6 atoms of aluminium they are again very steady temperatures. At H the alloy freezes homogeneously, it being the pure substance AuAl_2 . On adding more aluminium the curve descends rapidly to the eutectic point of gold dissolved in aluminium, the branch being, so far as we know, devoid of singularities. There is a short branch rising from this eutectic angle I to the freezing point of pure aluminium as shown in Curve 5.

The information given by the curves as to the compounds formed by the two metals may be summed up thus:—

Along the branch AB gold crystallises first.

Along the branch BC a compound crystallises first which is nearly pure at B, and is probably Au_4Al .

Along the curve CD a body crystallises first which is nearly pure at D, and is probably Au_5Al_2 , but may be Au_8Al_3 .

Along the curve DE the substance crystallising first is Au_2Al , a body of some stability which occurs pure at the summit E. The same body crystallises first along the branch EF.

Along the branch FG a new body crystallises first, but its formula is not given even approximately by the point G; it is perhaps AuAl .

Along the whole of the curve GHI the substance crystallising first is AuAl_2 , the remarkable and beautiful purple substance discovered and studied by Sir W. ROBERTS-AUSTEN.

So far as we have been able to see, the above are the only compounds indicated by the curve; but, owing to the rapidity with which the excess of red-hot aluminium attacks the porcelain cases of our pyrometers, we have not been able to determine the points on the curve HI with as great accuracy as the rest of the curve, and there might possibly be singularities in this branch, if it were not for the microscopical evidence against such a supposition.

We had much difficulty in determining the exact freezing point at the summit H, because the pyrometer tubes, after some hours' immersion in the alloy at 1000° , were very apt to become perforated, and hence to cause a change in the constants of the coils. But our best experiments, carried out with freshly made alloy, and with pyrometers in perfect order, which had immediately before been checked by the determination of the freezing point of gold, give the freezing point of the purple alloy at H, as identical with that of gold (see Curve 4). This coincidence is a remarkable feature in the relations of gold to aluminium, perhaps more remarkable than if the compound had frozen at a higher temperature than gold. It is impossible to misread the freezing points at H on account of the steady temperature.

SECTION II.

The Tables.

In column 1 of the table we give the number of the alloy in chronological order, in column 2 we state the percentage by weight of aluminium in the alloy as given by analysis, and in column 3 the atomic percentage. The numbers in square brackets are the percentages of aluminium based on a direct determination of both the gold and the aluminium. Column 4 contains the temperature of the freezing point on the platinum scale; this is CALLENDAR's *pt.* Column 5 contains the temperature of the freezing point on the Centigrade-air scale. In columns 4 and 5 the successive freezing points of the same alloy are placed under each other. In calculating the Centigrade temperature we strictly followed the method of calculation described in our paper "On the determination of high temperature" ('Journ. Chem. Soc.,' 1895, p. 160). Assuming, as we did, CALLENDAR and GRIFFITHS' value for the boiling point of sulphur, the δ of our platinum wire proved to be 1.50. If CHAPPUIS and HARKER's value for sulphur be taken, the δ will be slightly greater, and the melting point of gold will be raised a few degrees above 1062° , lower temperatures being raised by a corresponding amount. This correction can be made at any time, but as it does not affect the argument of the present paper, we have not thought it necessary to apply it. We give the platinum temperature *pt.*, that is, $100 \times \frac{R - R_0}{R_{100} - R_0}$ because this,

together with the fact that the ratio of R_{100} to R_0 is 1.385, enables the observed resistance to be re-calculated for an imaginary wire whose $R_0 = 1$. The symbols R , R_0 , R_{100} , are the resistances at the observed freezing point of the alloy, at 0°C . and at 100°C . respectively.

The number of the alloy referred to is placed before each note.

No. of alloy.	Percentage of aluminium by weight.	Atomic percentage of aluminium.	F.P., platinum scale [pt].	F.P., Centigrade. $\delta = 1.5$.	Notes.
0	0.00	0.00	909.0	1062.2	(0) Pyrometer 28. F.P. of 700 grammes Au.
1	0.30	2.14	896.2	1044.0	
2	0.66	4.62	873.7	1012.2	
3	1.04	7.11	843.9	970.7	
4	0.85	5.88	850.7	980.1	
5	1.27	8.56	806.0	918.9	
6	2.00	12.94	719.1	804.0	
7	2.74	17.02 [17.10]	601.2	655.9	(7) Upper F.P. very fugitive. Lower F.P. very steady, like eutectic.
			507.7	543.9	
8	3.85	22.57	493.1	526.9	
9	5.05	27.92	534.5	575.6	
10	6.20	32.50	573.7	622.5	
11	7.39	36.76	564.1	611.0	
12	7.88	38.39	551.2	595.5	
13	8.62	40.73	541.6	584.0	
14	9.91	44.48	574.8	623.9	
			528.7	568.7	
15	9.88	44.39	700.9	780.6	
			577.4	627.0	
			528.9	569.0	
16	12.19	50.27	761.9	860.0	(17) Pyrometer 28. F.P. of 390 grammes Au + 43 grammes Al.
			574.6	623.6	
			530.1	570.4	
17	9.78	44.12	601.2	656.0	
			574.1	623.0	
			528.0	567.8	
18	11.15	47.75	692.4	769.7	
			575.4	624.5	
			527.3	567.1	
19	11.76	49.25	736.3	826.3	
			574.6	623.6	
			527.4	567.1	
20	13.26	52.68	779.2	882.9	(21) Al. determined as sulphate.
			570.8	619.0	
			526.9	566.6	
21	14.76	55.77 [55.01]	823.8	943.1	
			571.1	619.4	
			526.6	566.3	
22	15.76	57.67	852.7	982.8	
			571.7	620.1	
			525.8	565.3	
23	16.75	59.43	874.7	1013.6	
			571.0	619.2	
			525.3	564.6	
24	17.68	61.00	892.7	1039.1	
			570.1	618.2	
			525.9	565.4	

No. of alloy.	Percentage of aluminium by weight.	Atomic percentage of aluminium.	F.P., platinum scale [°].	F.P., Centigrade. $\delta = 1.5$.	Notes.
25	19.57	63.92	906.3	1058.6	(25) The abnormal values of 25 and 26 are neglected in plotting the curve; they are almost certainly due to injury to the pyrometer.
26	20.50	65.26	569.8 526.3 912.2	617.8 565.8 1067.0	
27	20.51	65.27	905.1	1056.7	(27) Pyrometer 27.
28	21.46	66.55	907.7	1060.5	
29	20.69	65.52	905.9	1057.9	
30	22.11	67.40	907.4	1060.1	
31	23.86	69.54	905.7	1057.7	
			518.2	556.3	
32	26.63	72.55	899.3	1048.5	
33	28.40	74.29	888.7	1034.2	
34	32.70	77.97	874.3	1013.1	
35	36.13	80.46	853.4	983.9	
36	41.92	84.02	837.2 585.6	961.5 636.9	
37	41.93	84.04	837.2	961.4	(37) Pyrometer 25.
38	42.80	84.50	815.0	931.1	
39	45.36	85.82	792.7	901.0	
40	59.06	91.31	584.0 768.7	635.0 868.9	
41	92.45	98.90	593.5	646.5	(41) Pyrometer 21 gave immediately before this experiment the freezing point of pure aluminium as 654° C.
42	89.83	98.48	619.8	678.8	
			593.7	646.8	
43	84.88	97.63	646.8	712.2	
			592.1	644.8	
44	79.21	96.54	682.4	757.1	
			592.9	645.7	(46) Pyrometer broke down whilst searching for eutectic.
45	72.40	95.05	713.4	796.7	
46	65.39	93.22	754.3	849.9	
47	63.49	92.70	746.8	840.1	(47) Pyrometer 23.
			583.7	634.6	
48	57.53	90.80	770.0	870.6	(51) Pyrometer 23 in new tube. 584 grammes Au + 16.2 grammes Al.
49	50.14	88.00	799.3	909.8	
50	43.66	84.96	828.3	949.3	
51	2.72	16.92	603.4	658.6	
			507.7	543.9	
52	3.19	19.35	527.9	567.7	
			508.8	545.1	
53	3.54	21.09	500.2	535.1	
54	3.80	22.34	493.5	527.4	
55	3.95	23.05	507.9 492.4	544.1 526.0	

No. of alloy.	Percentage aluminium by weight.	Atomic percentage of aluminium.	F.P., platinum scale [pt].	F.P., Centigrade. $\delta = 1.5$.	Notes.
56	4.57	25.86	525.0 490.1	564.2 523.4	(60) Pyrometer put in new tube and constants found unchanged.
57	4.91	27.33	534.1	575.0	
58	5.54	29.93	552.8 533.1	597.3 573.7	
59	5.80	30.96	566.4 529.4	613.7 569.4	
60	6.35	33.06	574.6	623.5	
61	6.92	35.13	571.9	620.4	
62	7.42	36.85	560.9 528.2	607.1 568.1	
63	7.98	38.71	544.8 528.9	587.8 568.9	
64	8.94	41.69	545.6 529.5	588.8 569.6	
65	9.76	44.06	600.2 575.9 529.0	654.7 625.1 569.1	(67) Nos. 66 and 67 were successive extracts of the same alloy.* (69) Pyrometer constants redetermined and found satisfactory after putting in new tube.
66	12.57	51.15	780.8 573.7	885.1 622.5	
67	12.52	51.04	528.3	568.2	
68	15.56	57.30	864.0	998.5	
69	18.05	61.60	891.9	1038.0	
69A	19.58	63.93	898.5	1047.3	
70	19.91	64.41	902.3	1052.7	
71	21.44	66.53	904.9	1056.5	
72	22.58	68.00	905.2	1056.9	
73	23.61	69.24	905.2	1056.9	
74	25.31	71.17	901.7	1051.9	
75	2.93	18.02	564.5 506.8	611.4 542.8	(75) Pyrometer 13A. 584 grammes Au gave a freezing point 1061.4 (82) Pyrometer constants redetermined and found right.
76	3.53	21.04	499.2 494.9	534.0 529.0	
77	3.80	22.33	492.8	526.5	
78	4.06	23.55	508.8 491.9	545.2 525.5	
79	4.46	25.37	523.8 490.4	562.8 523.7	
80	4.88	27.19	533.9	574.8	
81	4.98	27.62	534.1	575.0	
82	5.55	29.96 [30.02]	559.2 532.4	604.9 573.0	
83	7.59	37.42	560.1 528.1	606.1 567.8	
84	8.02	38.83	548.1 528.6	591.8 568.6	
85	8.04	38.91	541.7 529.0	584.1 568.8	
86	8.25	39.57	536.6 529.0	578.0 568.9	

* In 66 the first and second freezing points only were determined, and in 67 the third or lowest freezing point.

No. of alloy.	Percentage of aluminium by weight.	Atomic percentage of aluminium.	F.P., platinum scale [<i>pt</i>].	F.P., Centigrade. $\delta = 1.5$.	Notes.
87	8.36	39.91	532.0	572.5	
88	8.80	41.27	529.0 541.4	568.9 583.7	
89	9.26	42.63	529.0	568.9	
90	9.50	43.30	565.3	612.3	
91	10.36	45.70	575.7 637.4 575.8	624.9 700.4 625.0	
92	20.50	65.25	904.7	1056.2	(92) Pyrometer 13A. F.P. Au 1062.5.
93	20.78	65.63	906.2	1058.3	
94	21.87	67.08 [66.65]	907.8	1060.6	
95	23.12	68.66 [67.95]	907.8	1060.6	
96	23.87	[69.70]	905.8	1057.8	
97	25.09	[71.30]	902.0	1052.3	
100	4.72	26.50 [26.59]	533.2	574.0	(100) Pyrometer 19. F.P. of Au 1062.6.
101	5.01	27.74 [27.91]	534.3	575.3	
102	5.22	28.63 [28.86]	542.4	584.9	
			534.2	575.2	
103	5.39	29.32 [29.13]	553.3	598.0	
			533.7	574.6	
104	5.89	31.31 [31.42]	569.7	617.7	
			528.4	568.2	
105	6.27	32.77	573.6	622.4	
106	6.50	33.61 [33.20]	575.2	624.3	
107	6.79	34.66 [34.89]	573.2	621.9	

TABLE showing the Freezing Points of Dilute Solutions of Gold in Aluminium.

Atomic percentage of gold.	F.P., platinum scale [<i>pt</i>].	F.P., Centigrade.
0.00	600.6	655.2
0.23	599.4	653.7
0.55	597.6	651.4
0.93	595.7	649.2
1.32	594.9	648.2
1.70	594.9	648.2
2.45	594.9	648.2

The higher freezing points of the last three alloys, that is to say, those lying on the branch III, were not determined.

SECTION III.

The Microscopic Study of the Alloys.

Sections, usually transverse, were cut from the rods of alloy extracted for analysis, and from other alloys, some of which had been slowly cooled. These sections were polished on graded emery paper and when necessary finished with rouge. They were then examined under the microscope both before and after etching. We found bromine water or aqua regia the only satisfactory etching reagents, these being about equally effective in developing detail.

Most of the reproductions in Plates 4 and 5 are from photomicrographs taken with an arc light, but in two cases, in which the photograph did not satisfactorily reproduce the detail of the object, we give drawings by Mr. E. WILSON of Cambridge, who has had a large experience in this kind of work. Except in the case of some low power photographs, for which oblique light was used, the illumination of the alloy surface was normal, a Beck's axial illuminator being used. The photographs are arranged in order according to the number of atoms of aluminium in the alloy, so that they can be readily referred to while reading the text; but reproductions are not given of all the alloys described.

However perfect photomicrographs may be, they rarely give as much information as a direct examination with the microscope. The descriptions which follow are therefore based on what was visible under the microscope rather than on the photographs, although we hope that the latter will confirm our statements.

The different ingredients of the alloys have, in some cases, well marked colours, but with different illuminants the tint of the same patch of alloy varies a good deal. It was therefore desirable to select a standard method of illumination for the eye examination. We employed a Welsbach gas-burner, an image of the flame being thrown a little out of focus on to the surface of the alloy. The colours of the various substances found in an alloy were then fairly constant, and could be employed as an aid in identifying them in different sections.

As a rule Zeiss' apochromatic lenses were employed, the powers ranging from 50 diameters to over 1000.

It will be seen that the microscopic examination confirms in every respect the information given by the freezing point-curve. The microscope reveals seven substances in the series of alloys, although they are never all found in the same alloy. They are gold and aluminium, pure at A and J, the ends of the curve, and four bodies which are nearly or quite pure at the points B, D, E, and H respectively. The seventh substance is present in all alloys between E and H, but never in a pure state. We shall sometimes refer to these as the B, D, E, H, and X bodies respectively.

Nearly all the alloys, when polished long enough on dry emery and rouge, acquire

a more or less golden tinge, and under the microscope show smears of gold, or a pattern of gold, on white or purple; and in cases where the polishing leaves a pitted surface, the pits are full of gold. On the other hand, the unpolished alloys are white if they contain more than 3 per cent. by weight of aluminium, except in the neighbourhood of H, where they are purple. This constant appearance of free gold on the polished surfaces troubled us a good deal at first, but we finally satisfied ourselves that most of it had been set free by the superficial oxidation of the alloys during polishing, and that after the oxidation of the aluminium the gold was smeared over the harder surfaces and rubbed into the pits. This, whether it be due to oxidation or not, can be to a large extent avoided by finishing the polishing on emery kept wet with benzene. The alloys are then almost free from gold smears, and we believe that in the solid unpolished alloys containing more than 20 atoms of aluminium, that is, after the point B, there is no free gold. This is an important point, for if free gold occurs to the right of B, the steps in the process of solidification become difficult to understand. One of the uses of the etching is to remove these smears of gold.

The types of pattern visible on the etched surface depend on the position of the freezing point in the curve. It is hardly too much to say that, given the freezing point-curve of any pair of metals, one can predict the microscopical structure of the alloys they form.

For alloys whose freezing point is near a summit of the curve, that is, near A, E, H, and probably J, the whole surface of the section is filled with one substance, although it is sometimes possible to detect fine boundary lines marking out the separate crystals. These lines are most often seen at the angles where three crystals meet, in which case (figs. 18 and 21) the boundary line consists of three branches meeting in a point.

When, by the addition of either metal, we leave a summit of the curve, the lines between the polygonal sections of the crystals become distinct, so that the pattern is that of a tessellated pavement, the unit being an irregular polygon, generally without re-entrant angles, often approximating to a regular hexagon, and often with somewhat rounded angles, so that it may be called a blob. It does not seem necessary to attribute the hexagonal shapes to any peculiarity of crystalline structure, but rather to the limitations of space in which the closely packed crystals have formed.* As we go further down hill along the curve, the spaces between the polygons widen and are seen to be full of a substance different from that of the polygons themselves. As we still go down-hill the interpolygonal matter becomes a continuous network, and the isolated polygons or blobs arrange themselves into patterns. Sometimes, as with 16.9 atoms of aluminium, the pattern is mainly one of rectangular crosses, but more often the blobs are in rows with other rows branching from them, the individual

* Mr. J. E. STEAD draws attention to the non-crystalline character of the shape of these polygons in his valuable paper on "The Crystalline Structure of Iron and Steel," in the 'Journal of the Iron and Steel Institute,' 1898.

blobs being often oval or elongated into bars as with 28.6 (fig. 16) and 29.9 atoms (fig. 17).

As we approach a minimum freezing point the rows of blobs become smaller in area, and the mother-substance around them, when examined with a high power, is sometimes seen to consist of a much smaller pattern of two substances, one being the material of the blobs. The 38.9 atom alloy (fig. 22) shows this well. Finally, at a minimum freezing point, a eutectic angle, the large blobs disappear entirely, and the whole alloy consists of the small pattern; it is a eutectic alloy. The 40 atom alloy (fig. 23) corresponding to the point F is an almost perfect example of this. If we now, by the continued addition of the same metal, cause the freezing point to rise, we again get large blobs surrounded by a minute pattern, but, while the fine pattern is the same as before, the blobs are of a different material; they consist of the second substance of the network (fig. 24). Thus in crossing from one side of a eutectic point to the other the two proximate constituents of the alloy exchange places.

If we think only of the plane surface of such a section of alloy as that with 29.9 atoms (fig. 17), the rows of blobs, each blob isolated from the next, yet obviously connected with it by some law, are puzzling. But if we think of the solid alloy as consisting of a mass of crystals with other crystals branching from them, the whole system immersed in mother-substance which solidified after the formation of the crystals, we see at once that a section of the mass would present the observed appearance. To be more precise, we may picture the 29.9 atom alloy during the first stage of freezing as like a thicket of fir trees in which the branches are at right angles to the stems and in which the stems are not all vertical. If a section were made of this thicket by a plane inclined to the vertical we should get patterns very like those of the photograph. If a stem lay in the plane of section we should get lines at right angles to each other. If the stem were parallel to the plane, but not in it, we should get parallel rows of dots. With the stem oblique to the section we should get the elongated dots which are so numerous in the photographs. A comparison of the X-ray photograph of the quickly cooled 96.6 atom alloy with the ordinary surface photograph of the same alloy illustrates the above. These considerations, together with the straightness of the lines of dots, show that the large pattern of blobs, and the polygons with which they are related, are the pure substance, which crystallised first and without constraint, because it was surrounded by liquid, whereas the surrounding matter is a mother-substance that was liquid during the first stage of crystallisation. It would be convenient to call the polygons and blobs primary crystals, inasmuch as they formed first in order of time, while the mother-substance may be said to contain secondary and tertiary crystals. It is probable that the marked absence of crystal form observed in the blobs of primary crystallisation is due to these blobs being what LEHMANN calls "crystal skeletons"; a snow crystal is the most familiar type of crystal skeleton. If we imagine the interstices between the fern-like pattern of such a crystal to be filled up by sub-

ordinate crystallisation of the same body, the original outline will become lost, and the final outline will be rounded as we see it in the photographs. Prolonged etching of the 18.1 atom alloy breaks up the surface of the blobs and partially reveals a structure that may be that of an original skeleton, although this structure is not altogether what we should expect in such a case.

We will now consider the alloys taken in order, starting from the pure gold end of the curve.

The first alloy examined carefully was that containing 1.27 per cent. by weight of aluminium, that is, 8.56 atoms. It has to the eye the appearance of gold, is soft, and does not polish well, and the unetched surface shows no detail. Etching with bromine water produces a very brilliant surface, and a 2 millims. immersion objective, with a power of 500 diameters, now shows it to be made up of approximately hexagonal polygons, apparently of gold, with an incomplete network of fine brown lines between them. We do not give a figure of this as it is identical with types that occur later in the curve, for example at E and H. BEHRENS, ARNOLD, ANDREWS, and all who have studied dilute solutions of one metal in another, have observed the same type of structure.

The alloy with 12.5 atoms similarly treated shows the polygons of gold somewhat rounded at the angles, and surrounded by much more of the brown mother-substance. This brown substance has a minute sparkle in it when examined with a power of 500. A power of 1500 and careful focussing showed this sparkle to be due to numerous spots, which sometimes appeared white; this is presumably the detail of the eutectic. In the photograph (fig. 1) the darker parts are the spaces full of eutectic, but the scale is too small to show the smaller detail.

The next alloy contained 16.9 atoms of aluminium. It was very white when polished by the wet method, and the microscope showed, before etching, golden crosses dimly visible on a white ground. When lightly etched, a power of 50 diameters brought out a beautifully regular pattern of rectangular crosses and bars on a dark ground that was finely mottled with gold. The ground was brown and the pattern generally golden, but under some conditions of etching the pattern seemed to be white, and many of the minute specks in the brown mother-substance seemed to be white also. A power of 1000 brought out very clearly the fact that the ground was a eutectic mixture. A slowly-cooled alloy, containing 18.1 atoms, of which we give a photograph (fig. 2), presented a very similar pattern, but on so large a scale that it was visible to the naked eye; the pattern in the slowly-cooled alloy was, however, always golden. Although we have mentioned the occasional whiteness of the pattern in the 16.9 atom alloy, we do not feel able to attach any importance to it, as it was probably due to some electrolytic action occurring during the process of etching.

Light etching with bromine water shows very clearly that the ground of the 18.1 atom slowly-cooled alloy is a eutectic mixture, as the gold is left standing up in bent rods and crinkles while the other substance of the eutectic is eaten away. We

give a photograph (fig. 3) of a patch of this etched eutectic taken between the bars of pattern so that no primary crystals are in the field. The somewhat cellular character of the eutectic strongly suggests three stages in the freezing, first, the formation of the large primary crystals of gold, then, probably after surfusion, the solidification of most of the second substance, and, finally, that of the residual gold in the interstitial spaces to form what becomes the minute raised pattern of the eutectic. Various other sections have suggested the same three stages. In the case of the slowly-cooled alloy with 18.1 atoms, the primary crystals or blobs, which are presumably gold, show a marked pattern after etching. Each blob, instead of being uniformly attacked by the etching agent, is eaten away into deep grooves running in various directions, and having no relation to the lines of polishing.* This, as we have said, may mean that the blob is not a crystal, but a mass of crystals; a longer etching reduces a blob to a cellular appearance very much like the drawing of the 19.8 alloy.†

With 19.4 and 19.8 atoms of aluminium we see a complete change in the pattern of the sections. Instead of the isolated primary crystals of gold, fairly uniformly scattered through a finely grained eutectic that constitute the pattern at 16.9 and 18.1 atoms, we now have, after bromine etching and with normal light, a dark brown or black surface finely reticulated by a system of slender golden lines that divide it up into cells (fig. 5). Thus the appearance is that of a nearly pure body, the material inside the cells presumably being that of the primary crystallisation, and the slender golden boundaries being the mother-substance that solidified last in order of time. The two alloys are very similar in appearance, but there is more of the golden network in the 19.4 atom alloy. The curve gives for this alloy two freezing points, at the upper of which primary crystals of gold should have formed, but the section polished was cut from a portion of the extract that had run out of the Jena pipette after removal from the crucible, hence it was the most fusible part, and probably had a composition nearer to B than the point recorded on the curve. Oblique illumination brings out the golden boundaries of the polygons much better than normal light, and

* In this and other cases where there seemed a danger of the scratches causing a false pattern, care was taken to polish by motion parallel to one direction, so that scratches might be easily recognised by their parallelism to this direction.

† *January 30, 1900.*—As the transition from the alloy with 18.1 atoms of figs. 2 and 3 to the 19.8 atom alloy of figs. 5 and 6 was a considerable one, we have lately made an intermediate alloy (fig. 4) containing 19 atoms of aluminium. This alloy was made by melting together in a sealed and vacuum tube of Jena glass appropriate amounts of the 18.1 atom alloy and of aluminium. This alloy, when slightly etched, showed a small number of very slender rows of dots of gold on a brown ground; it was evident that the primary crystallisation was much less in amount than that of the 18.1 atom alloy of fig. 2. The surface of the 19 atom alloy was then deeply etched by immersion for twenty-four hours in bromine water. The resulting surface, photographed by oblique illumination (fig. 4), shows very well the slender but very regular crystal skeletons of gold that exist in the alloy. Owing to the small amount of the primary crystallisation (due to nearness to the eutectic point) these skeletons have not filled up with gold, and so lost their crystalline form. Fig. 4 gives us much the same insight into the structure of the solid alloy as that afforded by fig. 30, the Röntgen ray photograph.

shows also another feature of both sections. This feature, of which we cannot at present see the explanation, consists in a much coarser polygonal structure, the whole area being divided by dark bands into spaces, each of which contains from ten to fifty of the smaller gold-edged cells. The width of the dark bands is about that of an average sized gold-edged cell, and the material of the bands seems to be that of the inside of the cells. Photographs of the 19·8 alloy, taken with oblique illumination, show the larger polygonal structure, but only very imperfectly that of the gold-edged cells; we, therefore, give a drawing of this alloy (fig. 5). These sections, when magnified 200 diameters, very much resemble the figures given by Professor ARNOLD ('Engineering,' February 7, 1896) for gold containing 0·2 per cent. of bismuth or silicon, that is, for a nearly pure substance.

Whatever the meaning of the larger polygonal structure may be, our immediate point is that the cells of dark material, for the most part isolated from one another, are primary crystals, probably of a body pure near B. Both of these sections are far more intelligible under the microscope than in the photographs. With careful focussing and a power of 1000 one sees that the golden network of the 19·8 alloy is, where it widens at the angles, a eutectic mixture of gold and dark not unlike the drawing, only far more minute.

The 19·8 atom alloy of fig. 5 was not one of the extracts made during the determination of the freezing point-curve, but was specially prepared for microscopic examination, it was, however, extracted from the crucible by sucking up in the usual way. We have since polished a section of the ingot left in the crucible after extracting this alloy. The ingot, of course, cooled much more slowly than the rod extracted. The polished section of the ingot shows before etching a cellular pattern, the cells being full of a uniform material, while the intercellular matter, or mother-substance, of which there is a good deal, broadening at the angles, is plainly a fine eutectic (fig. 6). A power of 400 diameters shows this well. This section, even when lightly etched with bromine, shows no trace of the larger polygonal structure. Both these alloys polished to very white surfaces. The rod of alloy from which the latter section was cut was white and brittle with a conchoidal fracture.

At 21·1 atoms we have, after bromine etching, the same brown polygons forming the mass of the alloy, but now the interstices are filled with a new white body, with which we shall become familiar later on. We give a drawing, under oblique illumination, of this alloy (fig. 7). The drawing accurately represents a portion of the surface, but is rather misleading as to the amount of interpolygonal matter, for if one takes a general survey of the surface one sees that there is very little of this. We give a photograph (fig. 8) to make this fact clear. Hence the alloy is extremely near to being a pure substance, nearer, for example, than the previous alloy. After the drawing was made, the section was subjected to a prolonged etching with strong bromine water. This brought out very clearly the white interpolygonal substance standing in relief above the level of the brown. This alloy before polishing was brassy-white with a

conchoidal fracture. Thus near B, on both sides of it, we find the structure characteristic of an almost pure substance.

The next alloy with 21.6 atoms shows a pattern that varies a good deal in different parts, but the most usual is that of armies of very minute dots and short lines of white in a ground which, after etching, is a golden brown. There are a few larger spots of white, so that we may have now just passed the eutectic angle C. In the middle of some of the brown spaces, between the bars and dots of white, a power of 1200 shows patches of a network of white lines, similar to that on the golden mother-substance of the 26.1 atom alloy to be referred to later; this is probably the real eutectic structure (fig. 9).

These features in the alloys, taken together with the shape of the curve between A and C, and especially the horizontal line of second freezing points at the temperature B, make it extremely probable that the solid alloy containing 20 atoms of aluminium is a homogeneous chemical compound with the formula Au_4Al . With rather more gold the solid alloy must consist of primary crystals of Au_4Al in a eutectic of this body and gold, the eutectic angle being probably near 19 atoms. With more gold we have, as at 18.1 atoms, primary crystals of gold immersed in a eutectic mixture of gold and Au_4Al .

With more than 20 atoms of aluminium we are on the new equilibrium curve BC, along which Au_4Al should crystallise first, and be found in the solid alloy embedded in a eutectic containing also the new white body D. Unfortunately we have not enough alloys on this branch, but the 21.1 atom alloy (figs. 7 and 8) unmistakably shows this white substance. As the rod of extract at 19.8 atoms shows, both before and after polishing, the body Au_4Al is itself a white substance, but it is very readily attacked by etching reagents, and therefore under the microscope it appears brown or purple from a film of gold.

As the alloy Au_4Al would contain only a little more than 3 per cent. by weight of aluminium, it is obvious that our analyses, though very consistent with each other, leave the exact atomic percentage at B a little indefinite; the method of plotting in atomic percentages may be said to magnify the scale of the curve here, on account of the disproportion between the atomic weights of the two metals. But we think it justifiable to use the law of multiple proportions in selecting the formula Au_4Al as that of the compound which is pure near B.

We have three sections of alloy containing 22.3 atoms of aluminium; they are all similar, and have a curious pattern. With a low power of 50 or 100 one sees dark polygons outlined not by lines but by small somewhat oval spots of white, which punctuate, as it were, the margin of the polygons. This is best shown in a section of a part of the alloy which ran out of the pipette after removal from the crucible. This must have been the most fusible part of the extract, and was therefore probably very near the composition of the eutectic C. With a higher power and the 2 millims. immersion one sees that these white spots have all the character of the D body, they

are a rough brilliant silvery white. Moreover they are rounded, and have no appearance of having been squeezed into the interstices of crystals already formed. So that it is hard to say which of the two ingredients crystallised first ; but the higher the power one uses the more disposed one is to say that the white spots were the primary crystals. With a power of 1000 or 1500 the ground shows a detail in it of small spots like minute grains of wheat, some of which are white. Probably this alloy represents the eutectic as fairly as that with 21.6 atoms.

With 23.1 atoms (fig. 10) the blobs of white are very uniformly distributed in a dark field, filling about one-third of it. They are a brilliant silvery pitted white. At 23.6 atoms the white blobs have increased in area, and form a beautiful object when examined with a low power. At 25.9 they fill two-thirds of the field (fig. 11), and are a remarkable example of rectangular crystallisation. At 26.5 atoms the white blobs have grown into elongated polygons, only separated by a broken network of dark lines ; in other words, the D body is nearly pure, the slowly-cooled 26.1 atom alloy (fig. 12) gives a good idea of these.*

This slowly-cooled alloy shows between the masses of white a network of golden-brown, which broadens at the angles. These broader patches of mother-substance under a power of 700 diameters prove to be full of minute polygons, bounded by bright, and often white, lines. This we presume is the structure of the eutectic corresponding to the state C. This mother-substance was formed after surfusion. The pattern is found on every patch of the mother-substance, although the boundary lines of the polygons are often incomplete (fig. 13). The section at 27.2 atoms (fig. 14) is very remarkable ; it consists, like the preceding one, of polygons separated by lines which are now fine and broken ; but the polygons are in groups, some of the groups being of a greyish-white rough substance, while other groups are a very smooth brilliant ivory-white. With oblique illumination the rough polygons show the effect of changing from bright to dark, as the stage is rotated through a right angle. Examination with a high power, however, forces one to the conclusion that the rough and smooth patches are of essentially the same material. The photograph of this section, with a magnification of 50 diameters and normal illumination (fig. 15), shows how very misleading a photographic reproduction may be. It does not give the impression of being the homogeneous substance that it really is. Even with a high power one cannot say to a certainty whether the interstices between the polygons are filled with the same eutectic as that found in the 26.1 atom alloy or with a new one : this point, if settled, would determine the formula of the D body.

At 28.3 atoms we have a complete change ; with oblique illumination, as in figure (fig. 16), one sees scanty groups of primary crystals of a new substance on a uniform ground. Some of the new crystals, examined with a power of 1000, show traces of

* This photograph was taken with oblique illumination, and the white and dark patches are of the same material differently orientated.

the door-panel moulding described later as characteristic of the E body. This alloy polishes to a fine white surface. We must have passed the intersection D of the branches CD and DE of the curve. The curve and the microscope here, as usual, agree very well, the upper fugitive freezing point being due to the small amount of the new primary crystals, and the lower very steady freezing point to the solidification of the large mass of mother-substance. As by adding aluminium we now pass up the curve towards E, the successive alloys show the primary crystals increasing at the expense of the ground, the 29.9 atom alloy being a good example (fig. 17), until at 32.5 atoms we have the new body in polygons separated from each other only by a fine ribbon network of a different material (fig. 18); and at the point E, close to 33.3 atoms, we have a practically pure substance.

The D and E bodies are white, both before and after etching, and each appears in two forms, according to the orientation of the crystals to the plane of section; one form is smooth, like milky ice or ivory; the other is uniformly pitted, or in some cases ruled with lines. It would seem that the crystals are made up of minute rods closely packed together,* and that section by a plane parallel to the rods gives a smooth surface, perhaps a cleavage plane of the crystal. On the other hand, a section making an angle with the rods breaks off each rod along another cleavage plane, which will not generally be that of the section, in which case the surface will be serrated or pitted. This way of accounting for the markings on a section of a mass of crystals has no doubt occurred to many persons;† but it was suggested to us by Professor EWING's slip-lines. He has shown that the minute elements of a crystal, even of metal, are rigid, and that they can only slip along certain planes. In the same way it is almost certain that they can only break along certain planes.

The remarkable effects that one often sees on rotating a section under oblique light are due to these serrations.‡ The fact that the pitted crystals give this *rotation* effect, shows that the sides of the pits have a definite orientation. The variation in the appearance of different crystals of the same substance, dependent on their orientation to the plane of polishing, is liable to mislead anyone who trusts to microscopic study only. For example, the alloy with 27.2 atoms photographed with normal light (fig. 15) appears to consist of at least two materials, while in reality all the patches in it are of the same substance; oblique light would be even more deceptive as the slowly-cooled alloy with 26.1 atoms (fig. 12) proves.

* An examination of the door-panel moulding of the alloy with 33.6 atoms almost forces one to the conclusion that these minute rods or laminae came into existence *during* the crystallisation, and are not a later product due to strain or other cause; that they are, in fact, the *crystals* of which the blob or polyhedron is built up. This is the view insisted on by Mr. STEAD (*loc. cit.*).

† Since writing the above we see that this is the view of the phenomenon given by Professor ARNOLD ('Engineering,' February 7, 1896).

‡ The nature and cause of this change of appearance when a section is rotated under oblique light is very clearly explained by Mr. STEAD (*loc. cit.*). He attributes the first mention of it to Professor ARNOLD. We shall call it the *rotation* effect, as no name appears to have been given to it hitherto.

The bodies D and E are so similar under a high power, that we found it difficult to believe them to be chemically unlike each other, but the form of the curve, and the relative positions of the two bodies in the sections examined, are both best explained by the hypothesis of their not being the same substance. The E body, which is most certainly Au_2Al , is in equilibrium with the liquid along the curve ED, while at D there is a triple point. This point corresponds to a temperature and concentration at which both solid bodies can exist in equilibrium with the liquid. At points between E and D we therefore have primary crystals of E immersed in white mother-substance. The door-panel moulding, distinctive of the E body, and described later, is found on the primary crystals as far back as 28.3 atoms. The mother-substance along DE is very white and uniform, and does not resolve into a eutectic mixture, but under the 2 millims. immersion it shows a tendency to break up into polygons, with thin lines between them. This can with care be detected in all sections, from 27 to 31 atoms of aluminium, and is just what we should expect to see if D, the intersection of the two branches CD and DE, lay a very little on one side of the summit of the branch CD.

While we are confident that the E body is Au_2Al , we cannot feel the same confidence as to the formula of the body which would be pure at the summit of the branch CD. The formula Au_8Al_3 would put the summit at 27.3 atoms of aluminium. This would fit in very well with the curve; and our alloy (fig. 14), which professes to contain 27.2 atoms, has, as the photograph shows, very little mother-substance between the polygons; that is, it is nearly a pure body. On the other hand, the formula Au_3Al_2 puts the summit of CD at 28.6 atoms. Alloys of this composition can be seen in the photograph (fig. 16) to have in them a small quantity of primary crystals of E, so that if Au_3Al_2 is the formula, the summit must lie a little underneath the branch DE, and be therefore unrealisable.

Before leaving the branch DE, the very rounded shape of the blobs of the primary crystals of E should be noticed. Their shape is just what one would expect to see if an emulsion of two conjugate liquids were suddenly solidified. We have been sometimes strongly tempted to think that E did separate in liquid drops along this branch. The same effect is seen, but not so strongly, along EF, and indeed in almost all the primary crystals, but such a supposition would leave unexplained the larger regular patterns in which the blobs arrange themselves, and we are disposed to think that, as we have already stated, the blobs are filled out crystal skeletons.

The alloy Au_2Al , which is pure at E, shows when examined with a high power, a great deal of detail. Many of the polygons are ruled with fine lines (fig. 19), the direction of ruling being often different in different polygons. These patches of course present the *rotation* effect. In many places it shows a beautiful crystalline structure with a pattern resembling the moulding of the panels of a door, and not unlike the well-known appearance of crystalline bismuth. We give a photograph of this (fig. 20) taken with a magnification of 450 diameters. Practically no eutectic is

visible between the crystal aggregates, but in some parts of the section the polygons are marked out by very fine lines; one polished section showed this before etching. The alloy itself is a somewhat brittle white substance. Etching with bromine or aqua regia develops large patches of various shades of grey, some very silvery: these are well seen with a hand lens. Oblique illumination, with a power of 50 diameters, shows groups of silvery spots on a dark ground. These spots disappear on rotation of the stage, and others become visible. The large patches also change from light to dark in the same way. As far as one can see, the whole surface shows this *rotation* effect, and consists of groups of polygons of the same substance in different orientations.

The alloys between E and G are a mixture in varying proportions of the above described Au_2Al and of the body named X. This latter, when unetched, is of a fine ivory white, but etching attacks it more rapidly than is the case with the E body, and turns it grey or brown. All the alloys between E and G are, when unetched, a mixture of pure white X and of E, which is often covered with gold. The effect of etching is to remove this gold and to show the pure white of Au_2Al , while the X body is darkened and rapidly eaten away. The alloy with 35.1 atoms (fig. 21) shows the smooth and the rough kinds of E and the door-panel moulding, and there is only a little mother-substance, the structure being that of a nearly pure body. The alloy with 36.6 atoms of aluminium, after etching with aqua regia, is shown, by a power of 50 diameters, to consist of silvery blobs almost isolated from one another. With a power of 500 this is a magnificent section. The white silvery spots of Au_2Al , each uniformly pitted, are surrounded by a eutectic consisting of a minute pattern of the same white, intimately mixed with the X body, which is grey or brown. With 38 atoms etched in the same way there are about equal amounts of the pitted form of E, and of the eutectic made up of E and X. The alloy with 38.9 atoms (fig. 22) shows a very good eutectic between the larger crystals of E. That with 39.9 atoms shows lines of silver dots of E, very slender, but beautifully rectangular in arrangement. The eutectic, which fills nine-tenths of the whole area, is resolved by a power of 500 into its two components. We are now very close to the eutectic point F, but still have a slight excess of gold. A slowly-cooled alloy, containing 40 atoms of aluminium, is the large scale but very uniform eutectic given in fig. 23. But one point of this alloy showed a primary crystal of Au_2Al that, magnified to the scale of the photograph, would be 2 inches across; this was the only primary crystal in the section. We mention its size to emphasise the relatively fine grain of the eutectic.

With 40.7 atoms the positions of the two ingredients are reversed; instead of the scanty rows of white spots of the alloy at 39.9 atoms, we now have a few very straight rows of spots of grey X immersed in the same eutectic. We have thus crossed over to the other side of the eutectic point F, and the X body is crystallising first. The alloy with 42.7 atoms, like all those between F and G, polishes well,

showing the X body in pure ivory white, and the network of eutectic somewhat in relief and golden from rubbed gold. When lightly etched, the X body shows in the form of grey blobs in a white and golden network; it is possible to entirely remove the gold, although at the risk of etching the X body somewhat deeply. The eutectic is somewhat coarse. With 43.3 atoms of aluminium the unetched surface shows only the usual pure white patches of X in a golden network. When lightly etched with aqua regia a power of 50 shows grey or brown blobs in a white network (fig. 24). With a still higher power the striated appearance of the dark blobs of X is seen. There are no traces of purple. A photograph of this is given in order that the relative amounts of X and the eutectic may be noted. We are practically on the horizontal line of freezing points running through G, yet the X body is very far from being the only substance present.*

Close to 44 atoms of aluminium we pass the point G, and an upper freezing point appears on the branch GH, so that the alloy has three freezing points. The microscope now begins to show crystals of purple in the alloy; at first very little, but as the percentage of aluminium increases, so does the amount of purple, until at H the alloy is pure purple. The photograph of the alloy with 51.2 atoms of aluminium (fig. 26) shows the isolated rows of crystals of the purple AuAl_2 . But in all the alloys between G and H there are three substances. This is well seen in the slowly-cooled alloy containing 45 atoms of aluminium, in which the detail is naturally large. A vertical section of this ingot of alloy contains a small amount of purple in large crystals near the top and on one side of the ingot, but most of the section consists of long-shaped isolated crystals of the X body in a network which is shown by a power of 20 diameters to be an exquisite eutectic of the E and X bodies. The photograph, before etching, of a horizontal section of this alloy (fig. 27) shows several dark crystals of the purple AuAl_2 , bordered by white X, and surrounding the large patches of white, the eutectic is seen. It is evident that the uppermost fugitive freezing point is due to the solidification of the purple AuAl_2 , that the well-marked freezing point at the G temperature marks the moment when purple ceases to form and the crystallisation of X begins. At this moment the still liquid part of the alloy has reached the composition given by G. As the alloy continues to cool, the liquid part traverses all the stages of temperature and composition corresponding to the points on the branch GF, crystals of pure X crystallising during this period. Finally, the residual liquid attains the composition of F, and the eutectic network forms at a constant temperature. The facts that the alloys between H and G are the only ones which plainly show three solid constituents, and that the solid alloy at G is a

* January 30, 1900.—An alloy whose analysis gave 44.1 atoms of aluminium, which therefore must be close to the transition point G, shows after prolonged etching with bromine water a very fine eutectic surrounding isolated spots of the primary crystallisation of X. A photograph of this is given in fig. 25. Figs. 22 and 25 are complementary; both contain the same eutectic, but the large primary crystals are in fig. 22 of Au_2Al and in fig. 25 of the X body, dark through etching.

mixture, not an almost pure substance like the alloys at B and D, somewhat differentiate the transition at G from those at B and D. The most probable explanation of what happens at G is that the curve FG, along which the X body is in equilibrium with the liquid, would, but for the formation of the purple alloy, be continued to a summit, X, on the right of G, and then no doubt downwards towards the aluminium end of the system. In the same way we must suppose that the equilibrium curve HG between the purple crystals and the liquid would, but for the existence of the X body, be continued below GF. Our experiments give, as is usually the case, only those parts of the two equilibrium curves which have no other branch above them. Our method of stirring the liquid vigorously until solid begins to form prevents very great surfusion and destroys any chance of finding freezing points on the hypothetical branch GX. But a cooling curve, conducted without stirring, might show such points. We have no conclusive evidence as to the formula of the X body, but as at G it forms considerably more than half of the alloy, the summit cannot be very much to the right of G; the formula AuAl seems to us an extremely probable one. The microscopical study of alloys near the point G shows how rash it would be to assume that an angle in a freezing point-curve, together with a horizontal line of second freezing points, necessarily gives the formula of a compound.

Alloys with more than 44 atoms of aluminium contain increasing quantities of purple the nearer we get to the summit H, at which point the whole area of the section is full of purple separated into large patches by slender lines of white that do not form a complete network. The alloy with 65.3 atoms of aluminium (fig. 28) shows the structure well. It is necessary to examine these alloys without etching them, as all etching reagents destroy the purple and cause an electrolytic deposit of gold on the other bodies present. Most of the alloys between G and H had been polished by the dry method, and hence the polished surface shows three things: the beautifully uniform crystals of purple AuAl_2 surrounded by the white X body, and, generally in the middle of the patches of white, some golden spots of eutectic. This eutectic is the matter solidifying under the conditions of the point F. As we have explained, the gold can be removed by wet polishing, in which case the eutectic is white, but distinguishable from the pure X. It appears to be the harder Au_2Al that retains the gold. Even at H the thin bands of X contain thinner lines and spots of eutectic. The purple is so generally surrounded by a border of pure white X, that the purple and the F eutectic are rarely in contact (fig. 27).

The alloys at 66.6 and 67.4 atoms have about the same amount of thread-like mother-substance, not more than 1 per cent. of the area, and at the latter percentage one does not see any marked change in the material of the threads. At 69.2 atoms the area of the bands of mother-substance has trebled at least, and it is greyer than at the same distance from the summit on the other side. At 72.6 atoms the mother-substance has of course increased, and it is now a soft greyish body full of scratches and quite unlike the substance X. Moreover these bands of grey have no threads of gold

running through them. This soft grey easily-scratched body increases in amount as we add more aluminium up to the end of the curve. The purple body seems to retain its character unchanged, although decreasing in area. With 99.3 atoms of aluminium one still sees small occasional spots of the unchanged purple, on the dirty grey ground, which is no doubt aluminium. Hence there is probably no new compound between H and the aluminium end of the curve. The alloys with more than 66.6 atoms of aluminium that were extracted for analysis polished so badly that we have not attempted to take photographs of them. But a specially made ingot of alloy, containing about 20 per cent. by weight of gold, that is 96.7 atoms of aluminium, was successfully polished (fig. 29). On the curve this alloy would be a little to the left of the eutectic angle I, and the pattern of the polished section naturally resembles that at a corresponding position on the other branches. It consists of rather scanty rows of small spots of the purple body arranged in straight lines at right angles to one another.

We give also a Röntgen ray photograph of a thin section of this alloy cut parallel to the surface of the previous section. This has been enlarged 5 diameters. In this shadow-photograph the opaque AuAl_2 is dark, while the eutectic ground, which is almost wholly composed of the transparent metal aluminium, is light. The resemblance between the pattern of the two is complete, but the Röntgen photograph naturally shows the numerous crystals in the body of the alloy as well as those on the surface.

Slowly-Cooled Alloys.

It might be thought that the rapidly-cooled samples of alloy extracted by the Jena pipettes would not give a fair picture of the character of the crystallisation of a more slowly-cooled mass. For this reason, and also to obtain larger detail, we prepared a number of slowly-cooled ingots of alloy by the method described in our paper on X-ray photography ('Journ. Chem. Soc.', 1898, p. 721). Each ingot weighed about 100 grammes. We found, however, that these ingots when cut and polished gave results identical with, though on a larger scale than, the quickly-cooled alloys. The slowly-cooled alloy containing 26.1 atoms of aluminium (fig. 12) shows by its marked *rotation* effect that the slow-cooling facilitates the grouping of the crystals into aggregates having the same orientations, and other slowly-cooled alloys confirm this. But as we have not found the slowly-cooled alloys contradict the evidence from the quickly-cooled ones, we do not give a detailed description of the former. There is, however, one exception to this due to the great difference in specific gravity of aluminium and the body AuAl_2 . A slowly-cooled alloy of these two substances, that is, one on the branch HI, will show a settlement of the heavy crystals of AuAl_2 to the lower part of the crucible. The Röntgen ray photographs (figs. 30 and 31) of the slowly- and quickly-cooled alloy, with about 96.6 atoms of aluminium, show this difference. We see in the photograph of the slowly-cooled alloy

that the very opaque AuAl_2 which crystallised first has settled to the bottom of the crucible, leaving a mother liquid which afterwards crystallised with the usual fine grain of a eutectic. The shape of the AuAl_2 crystals is distinctly visible in the negative, and is very similar to that of crystals of the same body in alloys between G and H.

The slowly-cooled alloy (figs. 32 and 33), containing 0.7 atomic per cent. of gold, is near the bottom of the branch JI, the quantity of AuAl_2 present is insufficient to saturate the aluminium, and, therefore, during the process of solidifying, the aluminium has crystallised first on the walls of the crucible, perceptibly concentrating the opaque AuAl_2 in the central portion of the ingot.

The Bodies B, D, E, X, and H.

The body B, pure at 20 atoms of aluminium, to which we attribute the formula Au_4Al , was obtained in the form of a brittle rod of white with a faint yellow tinge. It has a silky conchoidal fracture. Although containing little more than 3 per cent. by weight of the white aluminium, the colour of the gold is gone, in fact there is no free gold in it. This alloy is more easily attacked by etching reagents than pure gold, or than the D and E bodies, hence, after etching, we never see it as a white body but as yellow or brownish purple from a film of finely divided gold. D and E are pure white bodies, both before and after etching with bromine or aqua regia. Fused caustic potash dissolves out the aluminium from them and leaves them with a golden surface. They also break with a conchoidal fracture, and are hard and brittle.

The X body, which we think may be AuAl , has not been obtained pure in large masses, but a slowly-cooled alloy with 45 atoms of aluminium contains pure white patches of X; these are soft. The X body when in contact with Au_2Al is very rapidly attacked and eaten away by bromine or aqua regia, leaving a grey finely lined surface with the more resistant Au_2Al in relief.

The purple AuAl_2 is attacked by hydrochloric acid, a reagent which has little or no effect on the other bodies, the colour being destroyed and an electrolytic deposit of bright gold forming on the surrounding X body. It is curious that the compounds containing only a little aluminium should be white, while AuAl , with nearly 22 per cent. by weight of the white metal should have the splendid purple of finely divided gold. The identity in the melting point of AuAl_2 and of gold also marks out this compound as worthy of further study.

Eutectic Alloys.

As the photograph of the alloy with 40 atoms of aluminium shows, there is a typical eutectic at F. This alloy contains practically no primary crystals, but consists of two interlacing networks of E and of X, which must have crystallised almost simultaneously. It is an alloy of minimum and constant freezing point. This is probably the only section exactly at a eutectic point that we have polished, but there must be a eutectic corresponding to the point C, and also at a point a little to the left of B. But one can study eutectics in many other sections; an examination of the mother-substance between the blobs of primary crystallisation enables us to do this. For example, alloys between 36 and 40 atoms show the F eutectic very well, and it is also well seen here and there on the branch FG, and in the slowly-cooled 45 atom alloy a little above G. Again, although we have not absolutely located the eutectic point between A and B, yet the mother-substance of the 18.1 alloy shows the structure of this eutectic; the 19.8 atom alloy, which must be on the other side of the eutectic point, also shows a minute network in its golden mother-substance. The mother-substance of the branch CD, for example, at 21.6 atoms shows a eutectic mixture; but this was one of numerous cases in which surfusion preceded the solidification of the eutectic. One would expect surfusion to modify the pattern of the eutectic considerably, and, perhaps, to give three stages of solidification altogether, so that the eutectic structure would have that polygonal form characteristic of a nearly pure substance. The alloys on the branch DE show us that a *mother-substance* can be a pure body. This will occur whenever a branch of the curve cuts the next lower branch at the summit of the latter. The question whether a *eutectic* can be a pure body is really one of nomenclature. If we use the term eutectic for the mother-substance of the branch DE, the answer is, Yes; this mother-substance solidifies at a constant temperature, but is not an alloy of minimum freezing point.

The mother-substance along GH is a mixture, but not a eutectic. It, however, contains the F eutectic as one of its constituents; this is very well shown in the horizontal section of the 45 atom slowly-cooled alloy (fig. 27), the gold-smeared E of the eutectic having a minute pattern of pure white, X, scattered through it; this is, of course, in the unetched alloy. The quickly-cooled alloys of the branch GH do not always show the detail of the eutectic very well, but the row of very steady third freezing points makes the matter certain. The fact that these freezing points occur after marked surfusion may explain the scantiness of the F eutectic along the branch GH, and the fact that many of the blobs of E are large.

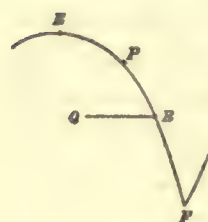
Summary.

The results obtained as to the equilibrium between gold and aluminium may be stated briefly.

Each point on the diagram of Curve 1 corresponds to a mixture of a certain composition at a given temperature.

All points above the curve correspond to homogeneous liquids. A point P on any branch of the curve corresponds to a state of possible equilibrium between a solid whose composition is given by the summit, real or imaginary, of the branch and a liquid whose composition is given by P itself.

A point Q below the branch of the curve, but above its lower end, corresponds to a mixture of a solid and a liquid. The composition of the solid is given by the summit of the branch, and that of the liquid by the point R, in which a horizontal through Q cuts the branch. An intersection of two branches, such as C, D, F, or G, corresponds to a state in which the two solids given by the summits of the two branches can both exist in equilibrium in the presence of the liquid given by the intersection point.



The phase rule for the case of two components in a system where the pressure is constant and the vapour pressure *nil* forbids the existence of more than three phases in true equilibrium. But the microscope shows that if an alloy containing 45 atoms of aluminium be cooled to the temperature of F, it must have contained the three solids AuAl_2 , X, and Au_2Al in contact with a liquid. This is true even in the case of slowly-cooled alloys; in other words, the purple AuAl_2 appears able to exist in the presence of a liquid that is not saturated with it. But the sections which present this paradox also give its explanation. In the slowly-cooled sections at 45 atoms the crystals of purple are always surrounded by a coat of the white X, which forms on them as soon as, by partial solidification, the state G is reached. Hence the crystals of purple take no part in the later equilibrium corresponding to points on GF.

The binary metallic system treated of in this paper has many points of resemblance with the system iodine-chlorine that has been already worked out. It illustrates general principles already accepted and adds nothing to them. But we hope it may have some value as a contribution towards the slowly accumulating proof that metals combine with each other according to the same laws that hold good for compounds not wholly metallic.

The metallurgist, moreover, who applies, as has already been partly done, the double method of this paper to pairs of metals likely to be of use in the arts would probably arrive at results of value to him.

We have to thank Dr. J. C. PHILIP for his untiring and most valuable assistance in

the experiments ; Professor EWING and Mr. ROSENHAIN for their kindness in advising us concerning the photomicrography, and for the loan of apparatus ; and Messrs. JOHNSON and MATTHEY for twice lending us considerable amounts of gold.

Much of the apparatus had been purchased at various times out of grants made by the Royal Society, and some by means of a grant made to us at the Dover meeting of the British Association.

GOLD-ALUMINIUM ALLOYS.

INDEX TO PLATE 4.

Fig.	Atomic percentage of aluminium.	Magnification.	Remarks.
1	12.5	100	Medium rate of cooling.
2	18.1	18	Very slow-cooling. Oblique light.
3	18.1	500	" " " Eutectic of 2.
4	19.0	45	Medium rate of cooling. Prolonged etching Oblique light.
5	19.8	250 (?)	Quick-cooling. A drawing under oblique light.
6	19.8	450	Medium rate of cooling. Vertical light.
7	21.1	(?)	Quick-cooling. Drawing under oblique light.
8	21.1	200	" " Vertical light.
9	21.6	1200	Medium rate of cooling.
10	23.1	60	Quick-cooling.
11	25.9	18	" " Oblique light.
12	26.1	4	Very slow-cooling. Oblique light.
13	26.1	1000	" " " Eutectic of 12.
14	27.2	120	Quick-cooling. Vertical light.
15	27.2	45	" " " "
16	28.6	45	" " Oblique light.
17	29.9	45	" " " "
18	32.5	120	" " Vertical light.
19	33.6 [33.2]	150	" " " "
20	33.6 [33.2]	550	" " " "

GOLD-ALUMINIUM ALLOYS.

INDEX TO PLATE 5.

Fig.	Atomic percentage of aluminium.	Magnification.	Remarks.
21	35.1	120	Quick-cooling.
22	38.9	120	" "
23	40.0	50	Very slow-cooled eutectic.
24	43.3	120	Quick-cooling.
25	44.1	120	" "
26	51.2	120	" " Not etched.
27	45.0	18	Very slowly-cooled. A horizontal section of ingot. Not etched.
28	65.3	60	Quick-cooling. Not etched.
29	96.6	18	" " " "
30	96.6	8	{ A "Röntgen" ray photograph enlarged.
31	96.6	2	Lower half of a very slowly-cooled alloy. A Röntgen ray photograph enlarged.
32	99.3	2	{ Very slowly-cooled. Vertical section of upper and lower halves of ingot. Röntgen ray photograph enlarged.
33	99.3	2	



Fig. 1.



Fig. 2.



Fig. 3.

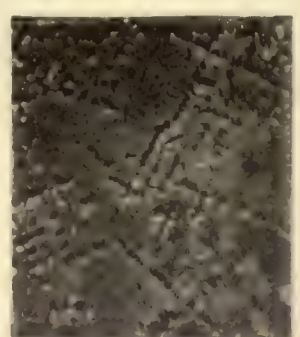


Fig. 4.

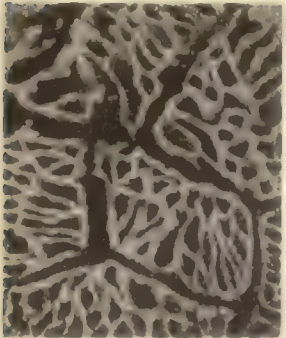


Fig. 5.



Fig. 6.

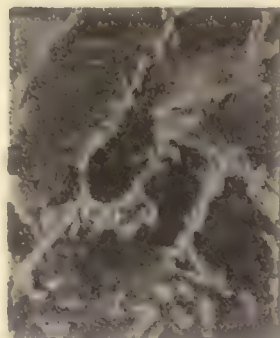


Fig. 7.



Fig. 8.



Fig. 9.

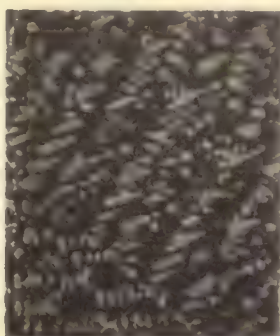


Fig. 10.



Fig. 11.



Fig. 12.

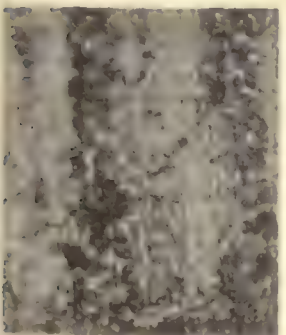


Fig. 13.

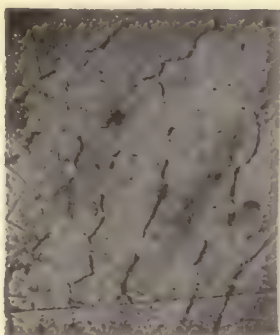


Fig. 14.



Fig. 15.

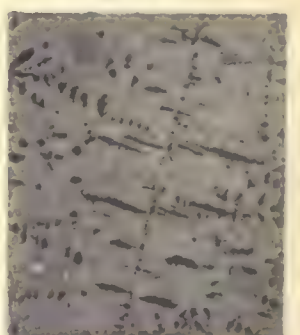


Fig. 16.

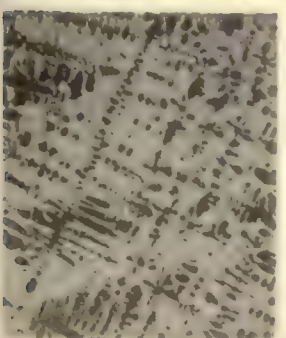


Fig. 17.

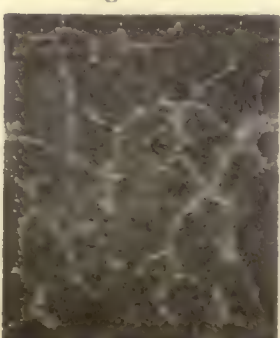


Fig. 18.

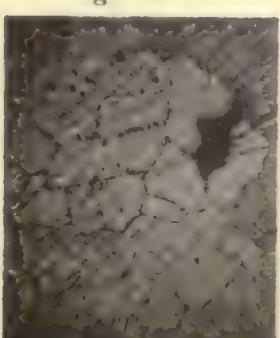


Fig. 19.

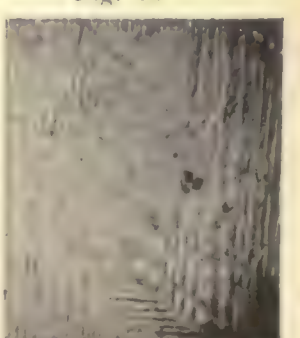


Fig. 20.

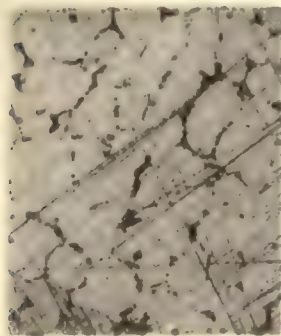


Fig. 21.

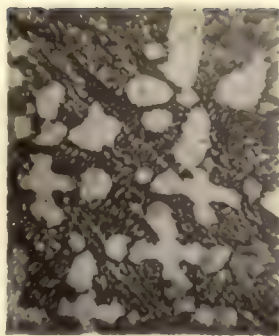


Fig. 22.



Fig. 23.

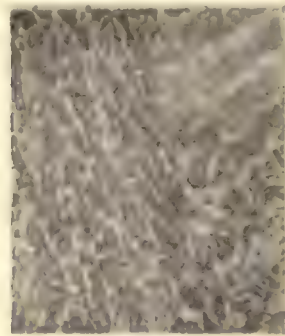


Fig. 24.

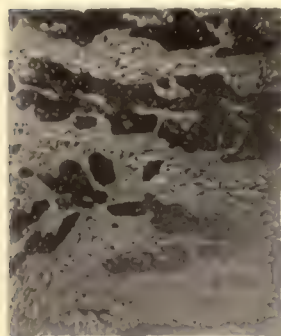


Fig. 25

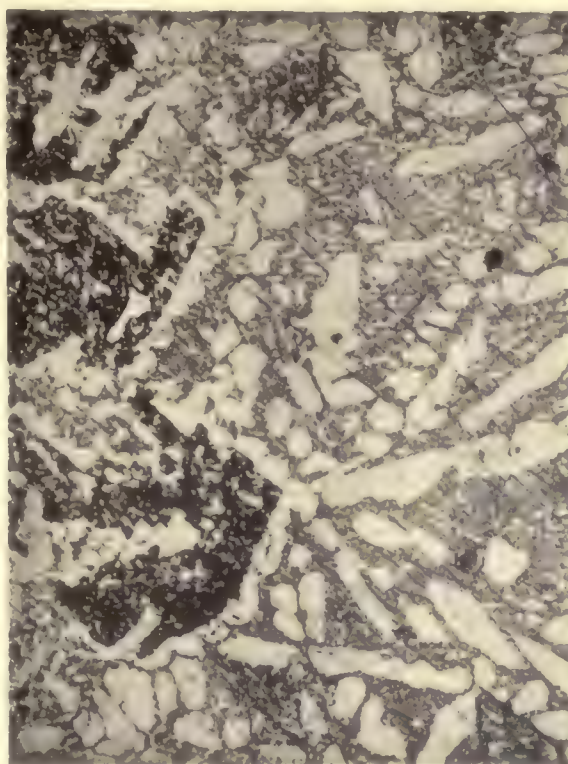


Fig. 27.



Fig. 26.

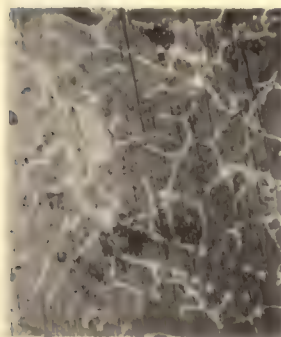


Fig. 28.



Fig. 29.

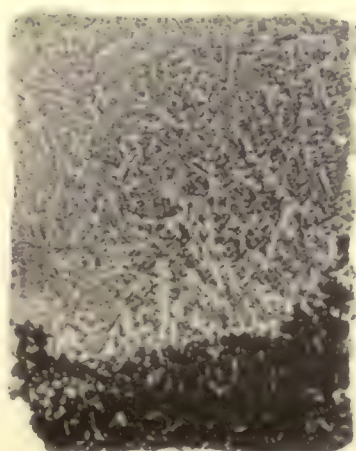


Fig. 31.

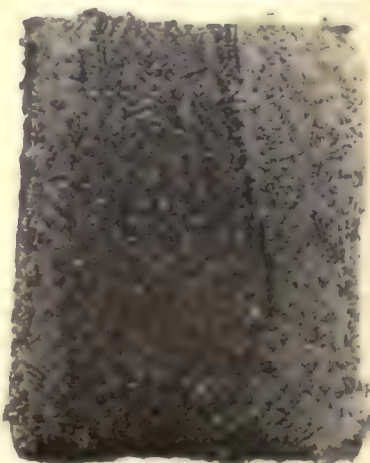
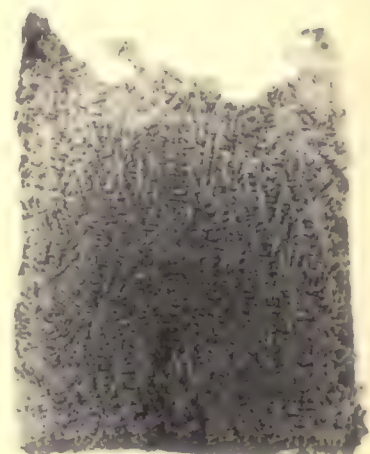


Fig. 33.

VI.—BAKERIAN LECTURE.—*The Specific Heats of Metals, and the Relation of Specific Heat to Atomic Weight.*

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With an Appendix by Professor JOHN PERRY, F.R.S.

Received February 9,—Read March 8, 1900.

THE experiments recorded in the following pages were begun nearly five years ago, at a time when opinion was still much divided as to the atomic weight of cobalt and nickel. It seemed to me that it would be a step in advance if it could be settled which of the two is the greater, for while perhaps the majority of chemists represented the atomic weight of cobalt as greater than that of nickel, some still assigned to them both the same value, while MENDELÉEFF* did not hesitate to invert the order by making Co = 58·5 and Ni = 59. After taking into account all the best evidence on the subject, it appears certain that the atomic weight of cobalt is greater than that of nickel, but the fact remains that the values differ from each other by an amount which is less than the difference between any other two well established atomic weights, the respective numbers being variously represented by different authorities as follows :—

	F. W. CLARKE.	T. W. RICHARDS.†	Committee of German Chemical Society.‡
	H = 1.	H = 1.	O = 16.
Co	58·55	58·55	59·0
Ni	58·24	58·25	58·7

The object of my experiments, however, soon developed into a wider field, for it appeared that the results obtained with these two metals might be made the means of further testing the validity of the law of DULONG and PETIT, inasmuch as temperatures at which the specific heats would be determined are not only very remote, but about equally remote, from the melting points of these two metals.

* 'Principles of Chemistry' (English translation, 1891), vol. 2, p. 333, and table at beginning.

† 'Amer. Chem. J.,' vol. 20, p. 543, 1898.

‡ 'Ber. d. Deutsch. Chem. Gesell.,' vol. 31, p. 2761, 1898.

Both metals are now obtainable in a pure state, and after melting and solidification under the same conditions are presumably in the same state of aggregation. Their atomic weights, though not known exactly, are undoubtedly very near together, as are also the densities of the metals and other of their physical properties.

The specific heats of cobalt and nickel were estimated by REGNAULT, using the method of mixtures, with the following mean results :—*

Nickel, '1090. Cobalt, '1067.

The metal in both cases contained carbon, and the cobalt probably contained nickel.

In the choice of the method for estimating the specific heat, my attention was drawn to the excellent results obtained by Professor J. JOLY in the use of his differential steam calorimeter.

It is unnecessary for me to describe the apparatus I have used, for it has been very carefully described by its inventor,† to whom I am greatly indebted for instructing the makers of the instrument in my possession. In using the instrument, all I have done by way of modification is to add a condenser for the escaping steam, and to take great precautions in determining the temperature of the space within the inner cylinder of the calorimeter by jacketing the thermometer and reading with a telescope; also in protecting the substance in the carrier from drip. The weights were all reduced to their equivalent *in vacuo*, due allowance being made for the exchange of the atmosphere of air for one of steam at 100°.

The following formulæ were used in the calculations :—

$$S = \frac{w\lambda}{W(t_2^\circ - t_1^\circ)} \dots \dots \dots (1),$$

where S is the specific heat, W the weight of the metal *in vacuo*, w the number of grams (or cubic centimetres) *in vacuo* of water condensed by the metal, t_1° the temperature of the calorimeter full of air before the admission of steam, t_2° the temperature of the steam in the calorimeter, and λ the latent heat of steam at barometric pressure; and

$$w = w_1 + w\delta - (V_1D - V_2\delta)$$

or

$$w = \frac{w_1 - V_1D + V_2\delta}{1 - \delta} \dots \dots \dots (2),$$

in which w_1 is the apparent weight in steam of water condensed by the substance, V_1 is the volume of the substance at t_1° , V_2 is the volume of the substance at t_2° , D is the density of the air at t_1° and barometric pressure corrected to 0°, δ is the density of the steam at t_2° and barometric pressure. A small correction (·0003 gram) had to be applied to one carrier to make it calorimetrically equal to the other.

* 'Ann. Chim. Phys.' [3], vol. 63, p. 23.

† 'Roy. Soc. Proc.,' vol. 47, p. 241.

The values for λ were taken from Professor JOLY's paper, those required being contained in the following abstract :—

Temperature and latent heat of steam.				
t° .			λ .	
99.37	to	99.48	536.9	
99.52	"	99.63	536.8	
99.67	"	99.78	536.7	
99.82	"	99.89	536.6	
99.93	"	100.07	536.5	
100.11	"	100.22	536.4	
100.25	"	100.36	536.3	

The value of δ was taken uniformly as .0006.

The first metal operated upon was a specimen of commercial sheet cobalt obtained from Messrs. WIGGIN, of Birmingham, for the analysis of which I am indebted to Mr. F. R. PENN, Assoc. R.C.S. It contained

Copper62 per cent.
Iron	1.92 ,,
Nickel	8.30 ,,
Carbon49 ,,
Cobalt (by difference) . . .	88.67 ,,
	<hr/>
	100.00 ,,

The specific gravity of the cobalt was 8.96.

The following data and results were obtained. The boiling temperature, t° , was usually taken from observation of the barometer.

W.	w_1 .	w .	t_1° .	t_2° .	S.
23.3580	.3544	.3530	22.64	100.07	.10480
23.3334	.3678	.3665	19.41	99.65	.10506
23.3105	.3768	.3753	18.00	99.93	.10550
23.3102	.3749	.3735	18.93	100.08	.10593
23.3111	.3688	.3675	19.43	99.82	.10523
23.2824	.3752	.3738	18.51	99.93	.10580
Arithmetical mean10539
Or omitting the first experimental ,, ,,10550
42.9247	.6828	.6803	19.48	99.96	.10565
42.9245	.6856	.6832	18.92	99.98	.10535
Arithmetical mean10550

These preliminary experiments showed that with a little practice it is possible to get results which are uniform to the third place, and could therefore be trusted as a basis for calculating the atomic weight if the pure metal were used.

Experiments on Pure Cobalt.

Preparation.—Commercially pure cobalt nitrate was dissolved in cold water and fractionally precipitated by the addition of weak solution of bleaching powder, leaving at least a quarter of the cobalt in solution. The oxide was collected, washed with hot water, dissolved in moderately strong hydrochloric acid, and the solution boiled to expel a part of the chlorine. Solution of ammonia was then added in excess, and the solution filtered through paper to remove a small brown precipitate containing iron and probably a little alumina.

The solution on being evaporated gave a deep red crystalline precipitate of purpureo-cobaltic chloride, leaving a pale mother liquor. The precipitate, drained, well washed with hydrochloric acid, and dried, was heated strongly in a platinum dish till fuming ceased. The dark blue crystalline mass of cobalt chloride was then dissolved in water and precipitated hot by excess of pure sodium carbonate. The precipitate was filtered off, washed, and heated to redness in a platinum dish. The resulting oxide was washed with hot water till free from alkali and dried. The oxide was then packed in a glass combustion tube and reduced at a red heat in pure hydrogen. The spongy metal was allowed to cool in hydrogen, and was then compressed into cylindrical blocks by a Spring compressor under a pressure of 64 tons to the square inch.

The rods thus formed were heated in a vacuum, when they gave off a little water and about their own volume of gas, consisting almost wholly of carbon dioxide, apparently absorbed from the air.

On exposing this metal to contact with steam and subsequently drying, it was found to increase appreciably in weight. Moreover, on attempting a calorimetric estimation with the metal, the first considerable increase of weight due to condensation of steam was followed by a small but continuous loss of weight, probably due to the slow expulsion of occluded gas. No accurate determination of specific heat was therefore possible. The metal was therefore supported upon a block of pure lime and melted in an oxyhydrogen flame. On the first attempt it was found that the melted mass on cooling ejected a considerable quantity of gas, giving rise to hollow excrescences upon the surface, the phenomenon closely resembling the expulsion of oxygen from melted silver in the process of solidification. After several experiments, it was found best to employ a considerable excess of oxygen at the end of the fusion, and though some loss of metal was incurred through oxidation of the fused button, much less escape of gas occurred on cooling. The buttons obtained were bright, but often hollow, the sides of the cavity being white and silvery. The metal breaks with a brilliant crystalline fracture.

A portion of the compressed but unmelted metal placed in a porcelain crucible and covered with glass was heated till the latter was melted and the crucible much softened. The metal in this case contracted visibly but was not melted, and it was preserved separately for a further attempt to determine the specific heat with the object of observing the difference, if any, between the melted and the unmelted metal.

Series II.

W.	w_1 .	w .	t_1 .	t_2 .	S.
Pure Cobalt. After fusion.					
21·9273	·3338	·3325	21·26	100·16	·10310
21·9311	·3258	·3245	23·50	99·99	·10378
21·9333	·3368	·3355	20·56	100·15	·10310
21·9314	·3266	·3253	23·14	99·99	·10355
21·9320	·3347	·3335	21·42	100·04	·10373
21·9377	·3310	·3297	22·33	100·13	·10362
Arithmetical mean					·10348
Pure Cobalt. Not fused.					
12·3493	·1848	·1840	22·52	99·96	·10323

The density of the fused cobalt was determined by weighing in benzene, the density of which was specially determined. Two experiments gave 8·7171 and 8·7191 respectively, or a mean of 8·7181 for the density of the metal at 21°/4°.

This cobalt was afterwards found to leave a minute trace of black substance on dissolution in nitric acid.

A fresh and larger supply of the metal was therefore made as follows: The purpureo-chloride was first prepared and precipitated from aqueous solution by adding strong hydrochloric acid, the precipitate being well drained, re-dissolved in boiling water, and again precipitated by hydrochloric acid. The salt was then heated in a platinum dish till converted into the anhydrous chloride, which was then transformed into sulphate, and finally into ammonio-sulphate by addition of pure ammonium sulphate. The double salt was crystallised from water in small crystals, which were well drained and washed. From a concentrated solution of this salt in water the metal was deposited by electrolysis, using as anode the cobalt of the preceding series of experiments.

After fusion in oxyhydrogen flame the metal gave the following values for the specific heat :—

Series X.

W.	w_1 .	w .	t_1 .	t_2 .	S.
17·1332	·2617	·2607	20·84	99·98	·10315
17·1332	·2582	·2573	21·81	99·98	·10306
17·1319	·2601	·2592	20·98	99·78	·10303
17·1317	·2590	·2581	21·15	99·74	·10289
Arithmetical mean.					·10303
Probable error					± ·000013

This result is very slightly lower than the result of the previous series.

Experiments on Pure Nickel.

For the metal used in these determinations I am indebted to the kindness of Dr. L. MOND, F.R.S. It had been deposited twice from the carbonyl compound by heating in a glass tube. It was afterwards found to contain a minute quantity of sulphur. In the form in which it was received it was, doubtless, somewhat porous, and when heated in a vacuum it gave off a small quantity of gas,* and this is probably the chief reason why the results obtained in estimating the specific heat are somewhat less uniform than those obtained with fused cobalt, and, as will be seen later, with fused nickel. The deposited but unfused nickel was not acted upon perceptibly by steam at 100°.

Series III.

Pure Nickel. Deposited from $\text{Ni}(\text{CO})_4$.

W.	w_1	w .	t_1 .	t_2 .	S.
22·1614	·3551	·3538	20·99	99·88	·10859
22·1605	·3592	·3579	19·87	99·96	·10820
22·1600	·3550	·3538	20·54	100·04	·10775
22·1601	·3545	·3533	21·32	100·29	·10829
22·1605	·3502	·3490	21·84	100·46	·10744
22·1618	·3516	·3504	21·58	100·12	·10798
Arithmetical mean.					·10804

* Ackworth and Armstrong found hydrogen in Russell's pure nickel, but not in fused commercial nickel nor in Russell's pure cobalt, though in the latter case it was surmised that hydrogen had been originally present, but the metal examined had undergone oxidation, all but the piece used in their experiments for solution in nitric acid, and which was "extremely dense and compact." ('Journ. Chem. Soc.,' 1877 [2], p. 82.)

The density of the metal was found to be 8·8759 and 8·8776, or a mean of 8·8768 at 21°/4°.

Pure Nickel. The same, fused.

W.	w_1 .	w .	t_1° .	t_2° .	S.
12·6668	·2001	·1994	22·95	100·06	·10953
12·6683	·2003	·1996	22·71	100·22	·10910
12·6671	·1997	·1990	22·78	99·93	·10926
Arithmetical mean					·10930

The density of the fused metal was slightly *less* than that of the unfused, namely, 8·7903 at 22°/4°.

This specimen was afterwards found to contain a small quantity of sulphur. It was therefore dissolved in nitric acid and converted into the double ammonio-sulphate, and this, after recrystallisation, was submitted to electrolysis, using an anode composed of fused Mond nickel. Its specific heat was determined after fusion.

Series XI.

W.	w_1 .	w .	t_1° .	t_2° .	S.
14·5414	·2275	·2267	22·30	100·22	·10732
14·5423	·2324	·2316	21·39	100·17	·10844
14·5421	·2266	·2258	22·88	100·15	·10779
14·5409	·2309	·2301	21·60	100·15	·10806
14·5425	·2294	·2286	22·30	100·15	·10831
14·5411	·2311	·2303	21·35	100·23	·10770

The results not being so concordant as was desired, the metal was cut through, as it was suspected there might be cavities, which would render the drying difficult. No cavities were observable, but in the succeeding experiments the metal was dried over sulphuric acid in an exhausted desiccator before use.

W.	w_1 .	w .	t_1° .	t_2° .	S.
14·0912	·2231	·2223	22·16	100·24	·10838
14·0919	·2238	·2230	21·88	100·10	·10852
14·0926	·2218	·2210	22·43	100·05	·10839
14·0930	·2247	·2239	20·90	99·89	·10791
Arithmetical mean					·10830
Probable error.					± ·00006

Finally, another specimen of nickel deposited from the carbonyl compound in Dr. MOND's laboratory was submitted to experiment. The whole was melted into a solid button free from cavities.

Series XII.

W.	w_1 .	w .	t_1° .	t_2° .	S.
15·1549	·2318	·2310	24·83	100·08	·10866
15·1535	·2379	·2371	22·52	100·10	·10818
15·1564	·2359	·2351	23·56	100·05	·10878
Arithmetical mean . . .					·10854
Probable error					\pm ·000047

The mean specific heats of pure cobalt and nickel after fusion may now be taken as follows :—

Cobalt ·10303 probable error . . . \pm ·000013

Nickel ·10830 } mean of means . . . ·10845
 ·10854 } with probable error . \pm ·000037

Arithmetical mean . ·10842

REGNAULT found the specific heat of cobalt made from the oxalate ·10696, and of nickel ·10863.

On multiplying these numbers by the atomic weights, the products are for cobalt $\cdot 10303 \times 58\cdot55 = 6\cdot03$, and for nickel $\cdot 10842 \times 58\cdot24 = 6\cdot31$, from which it is obvious that the atomic heats are not identical.

There is no other pair of metals so nearly allied together as cobalt and nickel, but with the object of testing the process further, gold has been compared with platinum and copper with iron, the atomic weights and densities in each case being pretty near together.

Gold and Platinum.—For the gold I am indebted to Professor Sir W. ROBERTS-AUSTEN. It was practically pure, containing, if anything, a minute trace of silver. It was supplied in the form of a rolled plate, and gave the following results :—

Series V.

Rolled Gold. S.G. 19·269 at 20°/20°.

W.	w_1 .	w .	t_1° .	t_2° .	S.
29·9920	·1395	·1386	18·27	100·10	·03029
29·9924	·1360	·1351	19·80	100·28	·03001
29·9924	·1362	·1353	19·80	100·19	·03010
Arithmetical mean . . .					·03013

The metal was then melted in a porcelain crucible by an oxyhydrogen flame applied outside.

Gold after fusion. S.G. 19.227 at 18°/18°.

W.	w_1 .	w .	t_1 .	t_2 .	S.
29.9886	.1432	.1423	17.23	100.60	.03052
29.9891	.1359	.1350	20.55	100.55	.03017
29.9892	.1396	.1387	18.75	100.46	.03035
Arithmetical mean03035

There is very little difference between the two series, the value after fusion being a little higher.

REGNAULT'S mean value for the specific heat of pure gold is .03244 by the method of mixture.

The platinum was prepared from scrap, chiefly foil. After successive treatment with hydrochloric acid, water, nitric acid, and washing, the metal was dissolved in aqua regia, the solution evaporated to dryness, and the residue was heated above 100 degrees for some time. The chloride was redissolved in water, the solution filtered, and excess of pure ammonium chloride added. The precipitate was bright orange yellow. It was washed with water, dried, and heated slowly to redness. The spongy metal was then compressed in a steel mould, and the resulting cylinders boiled in dilute hydrochloric acid, and then fused by an oxyhydrogen flame upon a support of pure lime. The buttons obtained were bright and lustrous, but the under surface which cooled less rapidly was blistered from the escape of gas. And from the specific gravity, which in various experiments was found to be 20.23, 20.33, 20.16, it was obvious that all were more or less permeated by cavities, although when this metal was heated to redness in a Sprengel vacuum it gave off no gas. Turnings obtained from one of these buttons had a specific gravity 21.323 at 18°/18°. After rolling one of them into a strip, it had a specific gravity 21.424 at 22°/22°.

Series VI.

Specific Heat of Platinum after fusion.

W.	w_1 .	w .	t_1 .	t_2 .	S.
29.0862	.1448	.1440	15.45	99.88	.03147
29.0860	.1405	.1398	18.16	100.00	.03150
29.0865	.1444	.1436	15.30	99.58	.03144
Arithmetical mean03147

The same Platinum rolled thin.

W.	w_1 .	w_2 .	t_1° .	t_2° .	S.
23.4692	.1158	.1152	17.30	100.12	.03177

REGNAULT's mean value for the specific heat of platinum by the method of mixture is .03243.

If we now compare gold with platinum

$$\text{S.H. of Gold} : \text{S.H. of Platinum} :: 1 : \frac{.03147}{.03035} = 1.0369.$$

In this case the atomic weights are known with a greater degree of certainty than those of cobalt and nickel. The value for the atomic weight of gold may be regarded as very accurately determined, while the atomic weight of platinum is still uncertain.

Assuming $\text{Au} = 195.74$ ($\text{H} = 1$), the atomic weight of platinum is $\frac{195.74}{.10369} = 188.8$, from which it is obvious that the law of DULONG and PETIT cannot be applied to such results in an absolute sense, for the atomic weight of platinum is approximately 193.41 (CLARKE).

Copper and Iron.—The copper was prepared by electrolysis from a solution of specially purified copper sulphate. After being washed and dried, the metal was fused in a covered ROSE crucible, supplied with a stream of hydrogen. The buttons on cooling gave off gas sufficient to produce a large cavity in each, but on afterwards heating to redness in a vacuum they yielded practically nothing. The metal was bright within and without.

Series IV.

Specific Heat of Copper.

Pure and after fusion. S.G. 8.522 at $20^\circ/20^\circ$.

Specific heat.

.09248

.09241

.09205

.09234

Arithmetical mean09232

Assuming the value 63.12 preferred by CLARKE for the atomic weight of copper, and the specific heats determined by REGNAULT and by KOPP, we obtain the following product of their combination :—

$$63.12 \times .09515 \text{ (REGNAULT).} \quad . \quad = 6.00$$

$$63.12 \times .0925 \text{ (KOPP).} \quad . \quad . \quad = 5.81$$

$$63.12 \times .0923 \text{ (W. A. T.)} \quad . \quad . \quad = 5.82$$

REGNAULT's copper on analysis gave "only traces of foreign matters." KOPP used "commercial copper wires."

The iron used in my first experiment was prepared by dissolving fine iron wire in hydrochloric acid, boiling the solution with nitric acid, and precipitating with excess of ammonia. The completely washed precipitate was dried and heated strongly in a platinum dish, then introduced into a glass tube and heated to redness in a stream of hydrogen made by dissolving aluminium foil in solution of caustic potash, and purified by passing through a moderately strong solution of potassium permanganate. The spongy metal was compressed into short rods in a steel cylinder, and then melted in an oxyhydrogen flame upon a support of lime. The buttons in solidifying gave off a considerable quantity of gas, presumably hydrogen. They were then rolled into moderately thin strips.

A sample analysed by solution in cupric ammonium chloride and combustion indicated 0.01 per cent. of carbon. This must be derived from atmospheric dust, as every precaution had been taken to exclude carbon compounds from the gases used in the preparation.

Iron in this state is apparently unaltered by contact with pure steam at 100°, but a small amount of rusting occurred during the subsequent cooling in the presence of atmospheric air.

The results were not as uniform as could have been desired, the two former experiments yielding results appreciably higher than the two latter. This may possibly be due to the presence of occluded hydrogen, which was gradually oxidised or expelled; at any rate no other explanation presents itself, as the experiments passed off successfully.

Specific Heat of Iron nearly pure and after fusion and rolling.

S.G. 7.75 at 18°/18°.

Specific heat.

·11022

·11037

·10946

·10926

Arithmetical mean . . . ·10983

The nature and amount of impurities present in a metal affect the value of the specific heat seriously. This is well known, and an instance is afforded by the results quoted at the beginning of this paper relating to impure cobalt. REGNAULT showed that the specific heat of a specimen of white cast iron, containing perhaps 6 per cent. of impurities, was ·12728, while that of malleable iron was ·11380. There are no data for estimating the effect of carbon by itself upon the specific heat of a metal,

but it might be expected to reduce the specific heat rather than raise it, as seems to be the case. In view of the uncertainty of the present state of knowledge, I have made some direct experiments upon the influence of impurities, the results of which are given briefly below. From these experiments it appears that the presence of a non-metal affects the result far more than the presence of a second metal, which produces very little effect upon the specific heat till the quantity of it is large enough to be felt through the difference of atomic weight (see Copper-tin). The influence of a *small* amount of carbon is proportionately much greater than the effect of a large amount.

Three samples of electrical iron, for which I am indebted to MESSRS. J. SANKEY and SONS, of Bilston, were then examined. Their composition is stated below. The metal was fused in the oxyhydrogen flame, as in all the previous experiments.

Sample A.	B.	C.
Carbon	·033	·030
Phosphorus	·020	·080
Sulphur	trace	·062
Silicon	·007	·040
Manganese	trace	·430

Percentage of non-metallic constituents.	S.H. experimental numbers.	Arithmetical mean.
A. ·060	$\left\{ \begin{array}{l} \cdot 11085 \\ \cdot 11101 \\ \cdot 11011 \\ \cdot 11104 \\ \cdot 11144 \end{array} \right\}$	·11089
B. ·105	$\left\{ \begin{array}{l} \cdot 11073 \\ \cdot 11010 \\ \cdot 11104 \\ \cdot 11070 \\ \cdot 11112 \\ \cdot 11050 \end{array} \right\}$	·11070
C. ·212	$\left\{ \begin{array}{l} \cdot 11134 \\ \cdot 11130 \\ \cdot 11134 \end{array} \right\}$	·11133

There seems to be no doubt that the presence of *non-metallic* impurities tends to raise the specific heat of a metal. Iron, however, is a metal which does not afford the best experimental material.

An attempt to discriminate between two samples of copper wire differing considerably in electrical conductivity failed, inasmuch as they gave practically the same

specific heats. For the samples and measurement of their resistances I am indebted to Professor AYRTON.

I. Specific resistance at $17.7^{\circ} = 2.75$ microhms per cub. centim. Analysed yielded no bismuth. Minute trace of antimony and .154 per cent. of arsenic.

Specific heat09266
„09267

II. Good copper. Specific resistance at $17.7^{\circ} = 1.69$ microhm per cub. centim.

Specific heat09274
„09272

Some specimens of copper to which phosphorus was added were then prepared, and the specific heat compared with that of the pure metal employed in their preparation.

Metal.	Specific heat.
Pure copper fused in hydrogen	{ .09265
	{ .09234
The same containing .002 per cent. phosphorus.	{ .09368
	{ .09336
„ .44 „	{ .09347
	{ .09320
„ 3.49 „	{ .09870
	{ .09910

The amount of phosphorus in each specimen was carefully determined after its preparation.

Some further data as to the effect of metallic or metalloidal impurity are provided in the following results:—

	Specific heat.
Copper, pure, fused in air, possibly containing oxide.	{ .0936
	{ .0938
„ with .49 per cent. tin.0936
„ „ 3.29 „	{ .0927
	{ .0924
„ „ „ „	{ .0905
	{ .0905
Cadmium, pure	{ .0556
„	{ .0553
„ with .2 per cent. of silver	{ .0561
	{ .0558
„ „ .1 „	{ .0554
„ „ „ „	{ .0558

The specific heat of a metal is affected by a variety of other circumstances, of which its mechanical condition is the most important. REGNAULT found the specific heat of hammered copper $\cdot 0935$ and that of annealed copper $\cdot 0952$. According to my results porous unfused metals all gave slightly lower values for the specific heat than the same after fusion.

As explained at the outset, all the determinations described up to this point were made in the steam calorimeter, and the results represent the average specific heats of the metals between the temperature of air, say 15° , and that of steam 100° . On applying the rule of DULONG and PETIT it has been shown that, notwithstanding the high degree of purity of the metals nickel and cobalt, the extreme care taken in determining their specific heats under the same conditions, and the close approximation of the physical properties of these two metals to each other, the numbers representing the atomic heats within the range of temperature of 15° to 100° differ appreciably.

The specific heat represents the relative amount of energy consumed in giving to the molecules of the solid the vibratory motion corresponding to temperature and in separating the molecules from one another, and so causing expansion. I am indebted to Mr. A. E. TUTTON, F.R.S., for determinations of the coefficients of expansion of the two pure metals, and his results have been published in the 'Proceedings of the Royal Society' (vol. 65, pp. 161 and 306). He finds the coefficient of linear expansion at t° for nickel $10^{-8} (1248 + 1.48t)$ for cobalt $10^{-8} (1208 + 1.28t)$, a difference of about 3.2 per cent. at 0° . His determinations also indicate that this difference increases with rise of temperature, and amounts to 4.3 per cent. at 100° . These differences of expansibility correspond very closely with the differences in the specific and atomic heats of the two metals.

I have also to thank Mr. THOMAS TURNER, Assoc. R.S.M., F.I.C., for observations with his sclerometer,* on the relative hardness of the two metals. He reports that the cobalt is harder than the nickel, the relative hardness being on his scale about Co = 17 and Ni = 12 or 13. The cobalt is harder than soft wrought iron, while the nickel is softer than wrought iron. The difference is therefore very distinct.

These differences of expansibility and of specific heat are the result of observations at and above atmospheric temperatures. As the specific heat of solids increases with rise of temperature and diminishes with fall of temperature, it was thought desirable to make some estimations of specific heat at successively lower temperatures in order to find out if the difference between the two metals was maintained. At absolute zero it is probable that they would exhibit the same capacity for heat, and if temperatures low enough could be employed an estimate could be made of the absolute atomic heat of the solid metals.

A series of calorimetric experiments has, therefore, been made at the tempera-

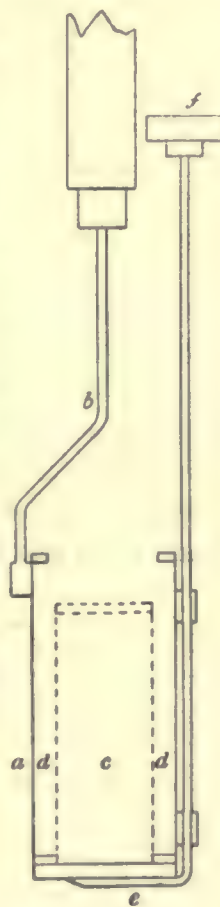
* 'Journ. Chem. Soc.,' 1885, vol. 47, p. 904; and 1887, vol. 51, p. 145.

ture of solid carbon dioxide, which was taken as -78.4° , and again at the temperature of boiling oxygen taken as -182.5° .

For this purpose a thin brass cylindrical vessel holding 400 c.c. of water, provided with an efficient stirrer in the form of a horizontal brass plate, perforated with rather large holes, was used. This calorimeter was supported by silk cords within a bright tin double-walled cylinder, the annular space being filled with water. The top of the tin casing was covered by asbestos card to prevent air currents, but arranged so as to allow the passage of the thermometer and the silk cord carrying the stirrer. The thermometer was divided into large tenths of a degree, and could easily be read to $.01^{\circ}$. The zero had been verified by ourselves, and it had been compared with a standard at Kew at each degree, the correction to the nearest $.01^{\circ}$ being supplied. So far as the observations of temperature in the calorimeter, the determination of the mass of water used and of the water equivalents of the brass, the thermometer, &c., were concerned, the usual procedure was adopted, and no details are necessary.

The problem of how to convey the cooled metal into the water of the calorimeter without appreciable heating in the air required a special contrivance. This is represented in the accompanying figure. The metal for experiment was placed in the interior, *c*, of a double brass tube, *a*, so constructed that the space, *d*, between the inner and outer tubes will hold liquid. The top of the inner tube, shown by the dotted line, is closed, while the top of the outer tube is open. The rod, *b*, by which the tube is held, is extended into a long wooden handle. The metal is retained in its place within *c* by means of a brass plate, *e*, working smoothly upon the mouth of the tube which it closes, and capable of being turned aside by rotating the head, *f*, of the rod which is attached to it at one side. The metal being introduced and supported by *e*, the holder was gradually plunged into liquid oxygen contained in a large cylindrical vacuum vessel till the double brass tube was completely immersed and the space, *d*, filled with liquid. The whole was left in the liquid till ebullition had practically ceased, or was proceeding at the same slow rate as the oxygen in a second vessel kept for comparison alongside. This happened in about 10 minutes after immersion. The metal was then assumed to be at -182.5° very nearly. On lifting out the brass holder the annular space between the two tubes remained full of liquid by which the temperature of the whole was kept down, and bringing the tube over the water in the calorimeter, the dish *f* was turned and the metal fell into the water.

The cold tube when brought into the air is of course attended by a cloud of cold air and mist which flows downward. In order to prevent the entrance of this mist into the calorimeter or its water-jacketed case a



stream of air was blown by means of bellows across the mouth of this vessel at the moment at which the cold tube was brought over it, and the metal dropped.

After reading the thermometer the calorimeter and its contents were weighed. The metal was previously weighed separately. All the weighings were reduced to a vacuum.

The following results were obtained :—

Expt. No.	Water + equivalent of calorimeter, &c.	Temperatures before, after immersion of metal at -182.5° .		Specific heat.
Cobalt, 39.15 grammes.				
1	415.74	13.33	11.79	.0842
2	414.29	12.75	11.27	.0808
3	414.09	13.81	12.30	.0820
4	413.84	13.88	12.37	.0819
Arithmetical mean . .				.0822
Nickel, 40.42 grammes.				
1	416.02	13.34	11.74	.0848
2	414.21	12.84	11.24	.0846
3	413.96	13.95	12.39	.0819
Arithmetical mean . .				.0838

Experiments at the temperature of solid carbon dioxide were carried out in a similar manner. The holder containing the metal was thrust into a cavity scooped out of a large mass (originally 50 pounds) of compact solid carbon dioxide, and the space between the inner and outer tubes was packed with the same. The apparatus remained in contact and surrounded by the solid for half-an-hour. The uniformity of the results which follow seems to prove that the metal had acquired the temperature of the cold mass.

Expt. No.	Water + equivalent of calorimeter, &c.	Temperatures before, after immersion of metal at $-78^{\circ}4$.		Specific heat.
Cobalt, 39.15 grammes.				
1	427.10	17.23	16.41	.0943
2	427.15	17.03	16.21	.0945
3	426.77	17.86	17.03	.0929
Arithmetical mean0939

Expt. No.	Water + equivalent of calorimeter, &c.	Temperatures before, after immersion of metal at -78.4° .		Specific heat.
Nickel, 40.42 grammes.				
1	424.75	16.13	15.25	.0987
2	424.40	16.49	15.62	.0971
3	424.05	16.99	16.12	.0966
Arithmetical mean0975

The mean specific heats of the two metals within three successive ranges of temperature now stand as follows :—

Temperature.	Cobalt.	Nickel.
From 100° to 15°	.10303	.10842
„ 15° „ -78.4°	.0939	.0975*
„ 15° „ -182.5°	.0822	.0838
and by calculation from the last two results		
From -78.4 to -182.5°	.0712	.0719

Mere inspection shows that the change in value proceeds regularly in both cases, but that the value for nickel declines more rapidly than for cobalt, and the consequence is that the specific heats of the two metals steadily approach each other. If the numbers given above for the specific heats are multiplied by the atomic weights, the products are very nearly identical.

Thus $.0822 \times 58.55 = 4.81$ atomic heat of cobalt, and $.0838 \times 58.24 = 4.88$ the atomic heat of nickel.

Or $.0712 \times 58.55 = 4.169$ and $.0719 \times 58.24 = 4.187$.

* Other recorded attempts to determine specific heats at low temperatures are as follows :—

Metal.	Temperature.	Sp. heat.	Temperature.	Sp. heat.	Authority.
Lead . . .	100° to 10°	.03140	10° to -77.75°	.03065	Regnault.
Platinum . .	100° „ 20°	.03295	20° „ -78°	.03037	Schuz.
Tin . . .	100° „ 20°	.05564	20° „ -78°	.05416	„

The falling off is in each case less than in my experiments, but the probability is that in these old experiments the metals were not really at the low temperature assumed when introduced into the calorimeter. (See note, p. 250.)

Hence the absolute "atomic heat" of the two metals, cobalt and nickel, is almost exactly 4.

It appears probable, therefore, that if the experiments could be carried further the specific heats would stand in exactly the inverse ratio of the atomic weights.

It remains to be seen whether the value of the atomic heat for other metals agrees with this.* If such turns out to be the case the original expression of the law of DULONG and PETIT, which is only roughly applicable at atmospheric and higher temperatures, would be completely justified.

In conclusion I desire to record my appreciation of the skilful assistance I have received throughout these experiments from Mr. SIDNEY YOUNG.

APPENDIX BY PROFESSOR JOHN PERRY, F.R.S.

Dr. TILDEN has asked me to write the following short appendix to his paper. In making the tedious calculations I was assisted by two of our students, Mr. E. R. VERITY and Mr. H. L. MANN.

The law connecting the p , v , and t of unit mass of any substance in the solid condition is not sufficiently well known for the general application of the laws of thermodynamics.

If we take it that there is an atomic or molecular specific heat k_0 of an elementary substance which is constant in all states of the substance, and which is represented

* *Note added March 3.*—Experiments made since this paper was written, upon the metals silver, copper, iron, and aluminium show that further investigation is necessary. The mean specific heat of silver, for example, was found to be $\cdot 0558$ between 100° and 15° , and $\cdot 0519$ between 15° and $-182\cdot 5$. The decrease of specific heat at the lower temperature is, therefore, much less than in the case of cobalt and nickel.

A paper by U. BEHN in the 'Annalen der Physik' (No. 2 for 1900, p. 257), issued on Feb. 16, did not come into my hands till some time after the date of my communication to the Royal Society. My attention was drawn by this paper to the fact that in 1898 the Author had commenced a series of determinations of the specific heats of metals at low temperatures, and that about the same time some experiments on the specific heats of three metals,—copper, iron, and aluminium,—at the temperature of liquid air, had been published by C. C. TROWBRIDGE in the American periodical 'Science' (N.S. 8, p. 6, 1898).

The results of the latter cannot claim to be very important, as no information is given concerning the composition of the metals, and there is great uncertainty about the temperature of the liquid in which they were cooled. The numerical values given by TROWBRIDGE are considerably higher than those of BEHN, as also in the one case, aluminium, in which a comparison can be made with my results; the mean specific heat between the temperature of air and that of boiling oxygen being $\cdot 1833$ according to TROWBRIDGE, and $\cdot 1676$ according to my experiments.

BEHN's results are highly interesting, though for various reasons they must be inaccurate in some cases and are probably to a slight extent inaccurate in all; inasmuch as no special means were taken to avoid access of heat in transferring the mass from the cold bath to the calorimeter, and as liquid air was used instead of liquid oxygen, the temperature of the cooling liquid was somewhat uncertain.

by its specific heat at constant volume when in the state of a perfect gas. If α is its atomic weight, then

$$\alpha k_0 = 2.414$$

for all elements, because it is of this amount for hydrogen.

Thus if $\alpha = 58.55$ for cobalt, and 58.24 for nickel, $k_0 = .04123$ for cobalt, and $.04145$ for nickel.

It is, perhaps, not unreasonable to assume that in no state can the substance have a smaller specific heat than this atomic specific heat.

If the specific heat of a substance at constant volume is k , and at constant pressure K , it is interesting to note that K and k are very nearly equal for solid metals, and, indeed, that the heat required to raise a gramme of solid metal 1° in temperature is not very different under all ordinary conditions as to pressure and volume. The ratio of K to k is known to be the ratio of the elasticity at constant entropy to the elasticity at constant temperature, or what we sometimes call the *quick* and the *slow* elasticity. The slow may be measured with a piezometer, or calculated from YOUNG'S modulus and the modulus of rigidity, the quick may be obtained from sound vibration experiments.

Thermodynamics of a Solid.

If we say that α is the real coefficient of expansion under constant pressure, we mean that

$$(dv/dt) = \alpha v.$$

When we say that ϵ is the volumetric elasticity at constant temperature, we mean that

$$(dv/dp) = -v/\epsilon.$$

In all probability α and ϵ are functions of the temperature, and practically of nothing else.

The thermodynamic coefficients become, all energy being measured in ergs,

$$K - k = \alpha^2 \epsilon v t,$$

$$l = \alpha \epsilon t,$$

$$L = -\alpha v t,$$

where K is specific heat at constant pressure, and k is specific heat at constant volume, and the significations of l and L are given by the following expressions for the heat, dH given to unit mass of the stuff when its t , p , and v become $t + dt$, $p + dp$, and $v + dv$.

$$dH = k \cdot dt + l \cdot dv = K \cdot dt + L \cdot dp.$$

Mr. TUTTON has measured what are ordinarily known as the coefficients of expan-

sion of pure nickel and cobalt with temperature. We have taken his observed numbers, and found what may roughly be taken to be the *true* coefficient of cobalt. As he had only two changes of temperature, we are compelled to assume that α is a linear function of the temperature, and we find

$$\alpha = (2.598 + .003775t)10^{-5}$$

We can therefore say that the heat (in gramme-centigrade degrees) given to 1 gramme of cobalt during an increase of temperature dt , and an increase of pressure dp , is, taking JOULE'S equivalent as 4.2×10^7 ergs,

$$dH = K \cdot dt - (6.186 - 0.008988t)t \cdot v \cdot 10^{-13} \cdot dp.$$

If instead of change of state being expressed in terms of dt and dp , it is expressed in terms of dt and dv , we can only use this result if we can calculate dp . This needs a knowledge of ϵ , which we do not possess for either cobalt or nickel, even at one temperature. It is, however, worth while making the following rough approximation.

In pounds per square inch ϵ is, for iron, 2.1×10^7 (KELVIN'S article on Elasticity); for copper, 1.7×10^7 (BUCHANAN); and 2.4×10^7 (KELVIN'S Elasticity).

We cannot do better in making a first approximation than to take ϵ for solid cobalt as 2×10^7 lbs. per square inch, or in C.G.S. units

$$\epsilon = 1.38 \times 10^{12} \text{ degrees per sq. centim.}$$

under all conditions.

We shall not be far wrong in assuming that, within Dr. TILDEN'S range of temperature, the above value may be taken for α .

Mean temperature of each range.	α .	v .	t .	K/k .
57.5° C.	38.45×10^6	.1149	330.5	1.018
-31.7° C.	35.1×10^6	.1145	241.3	1.012
-83.7° C.	34.4×10^6	.1143	189.3	1.010

We have taken v at 21° C. as $1 \div 8.7181$, or 0.1148 cub. centim.

In each case, therefore, it is easy to find $K-k$, or $\alpha^2 \cdot \epsilon \cdot vt$, which must be divided by JOULE'S equivalent 4.2×10^7 , to convert the specific heats from ergs to heat units. The last column shows that the two specific heats are nearly equal.

It is interesting to note, not merely in cobalt and nickel but in any metal, that if we take K to be either the specific heat at constant volume or pressure, the ratio of K to k_0 is very large at ordinary temperatures. Thus taking values from the tables prepared by Professor GRAY for the Smithsonian Institute :—

Substance.	^a . Atomic weight.	k_0 .	K.	K/k_0 .
Cu at 17° C. . .	63·6	·0378	·0924	2·444
" 100° C. . .			·0942	2·492
" 200° C. . .			·0963	2·548
" 300° C. . .			·0985	2·605
Pb at 15° C. . .	206·9	·01167	·0299	2·563
" 100° C. . .			·0311	2·665
" 200° C. . .			·0324	2·841
Ag at 23° C. . .	107·9	·02247	·0550	2·447
" 100° C. . .			·0566	2·520
" 200° C. . .			·0588	2·617
" 300° C. . .			·0609	2·710

These values are given for cobalt and nickel in a table below.

Our ignorance of the molecular state of a solid is so great that we cannot even speculate on how it is that when 1 gramme of cobalt at 50° C. rises in temperature to 51° C., whether it is allowed to expand freely or is subjected to great hydrostatic pressure which prevents expansion, the energy ·041 enters it as what may be called the real sensible heat, and the energy ·062 (or one and a half times as much) enters it as some kind of energy of disgregation necessary because of change of temperature and having nothing to do with change of volume or pressure. The facts are not explainable by assuming that the atomic weights are wrong, because as we see from cobalt and nickel, K approaches the value k_0 at low temperatures.

A table of temperatures may be made out at which for all metals the product of atomic weight and specific heat has any constant value. Thus we take it that at -273° C. this product is the same as it is for hydrogen or any elementary gas. At the following temperatures the product is 2·6 times what it is for hydrogen, and the product of K and atomic weight is in every case 6·28.

	Lead.	Copper.	Silver.	Nickel.	Cobalt.
Temperature . .	50° C.	290° C.	180° C.	52° C.	167° C.

We have no doubt if we had information to prepare exact tables of this kind (dealing with k/k_0 rather than K/k_0) we should find these temperatures related to other physical properties.

Dr. TILDEN'S measurements of the mean specific heat of cobalt and nickel in the following ranges of temperature are :—

Range of temperature.	Cobalt.	Nickel.
100° C. to 15° C. . . .	·1030	·1084
15° C. to -78·4° C. . .	·0939	·0975
15° C. to -182·5° C. .	·0822	·0838

We know so little of the molecular constitution of solids that any empirical formula which we may use for the calculation of the actual values of K , the specific heat, must be regarded as having no application higher than 100° C. and lower than -182·5° C. ; nor indeed can it have much correctness near these limits.

We have used $K = a + bt + ct^2$, and found the best values of a , b , and c for calculating K from the given mean values ; but we find that according to this law K both for cobalt and nickel reaches a maximum at 167° C. and rapidly diminishes for higher temperatures, and this is certainly wrong.

As it is possible that K is always greater at higher temperatures we were tempted to use

$$K = a + \frac{bt}{1 + ct}$$

But a came out negative. Now as a is the value of the specific heat at -273° C. or $t = 0$ we cannot imagine it ever negative. Indeed it is probably never less than k_0 the atomic specific heat. We therefore tried

$$K = k_0 + bt + ct^2 + et^3,$$

but the values of the constants are such that this causes K to reach a maximum at 270° C., and rapidly diminish afterwards.

To satisfy all our notions we know of better formulæ to use, but the labour of calculating the constants of these more promising formulæ coming after our other failures seemed too great.

We have, however, found a formula, easy to use, which fits Dr. TILDEN's results with some accuracy, which gives $K = k_0$ when $t = 0$, and which causes K to continually increase with temperature. It is of the form

$$K = k_0 + \frac{bt^3}{1 + ct^3}$$

	Cobalt.	Nickel.
k_0	·0412	·0415
b	$1·764 \times 10^{-8}$	$1·764 \times 10^{-8}$
c	$2·55 \times 10^{-7}$	$2·35 \times 10^{-7}$

In all probability these formulæ give fairly correct values of K from -180°C. to 100°C. In spite of the danger of extrapolation, we give in the following table some values beyond this range, to show that the formula expresses the sort of change known to occur in metals generally at high temperatures. Close to the zero there must be greater doubt as to its suitability:—

$\theta^{\circ}\text{C.}$	$t.$	Cobalt.		Nickel.	
		$K.$	$K/k_0.$	$K.$	$K/k_0.$
1327	1600	·1103	2·677	—	—
727	1000	·1101	2·673	·1162	2·801
527	800	·1098	2·666	·1159	2·794
327	600	·1092	2·651	·1151	2·774
127	400	·1063	2·580	·1119	2·696
77	350	·1046	2·539	·1098	2·646
27	300	·1016	2·465	·1038	2·501
— 23	250	·0965	2·342	·1005	2·422
— 73	200	·0876	2·126	·0905	2·181
— 123	150	·0732	1·776	·0747	1·800
— 173	100	·0552	1·340	·0558	1·345
— 223	50	·0433	1·051	·0436	1·051
— 253	20	·0413	1·002	·0416	1·002
— 273	0	·0412	1·000	·0415	1·000

[April 27, 1900.—The following formula reproduces Dr. TILDEN's results with greater accuracy. It is probably of a nature to suit all metals which exhibit no recalescence effects.

$$K = k_0 \left(1 + \frac{bt^n}{c + t^n} \right)$$

when the values of the constants for nickel and cobalt are

	Cobalt.	Nickel.
k_0	·0412	·0415
b	1·695	1·892
c	$1·002 \times 10^6$	$0·932 \times 10^6$
n	2·73	2·68

VII. *On the Association of Attributes in Statistics: with Illustrations from the Material of the Childhood Society, &c.*

By G. UDNY YULE, *formerly Assistant Professor of Applied Mathematics, University College, London.*

Communicated by Professor KARL PEARSON, F.R.S.

Received October 20,—Read December 7, 1899.

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I.—INTRODUCTION.

§ 1. In the ordinary theory of statistical correlation, normal or otherwise, we are always supposed to be dealing with material susceptible of continuous variation, or at least of variation by a *considerable number* of discontinuous steps. The correlations of lengths or measurements on portions of the body form examples of the first kind; of numbers of children in families, petals or other parts of flowers, are examples of the second.

Certain practical cases arise, however, where either no variation is thinkable at all, or else is not measured or possibly measurable. We may class a number of individuals into deaf and not deaf, blind and not blind, imbecile and not imbecile, without attempting to go further (although gradations of deafness, blindness, and imbecility occur), and demand on the basis of the enumeration a discussion of the *association** of the three infirmities. Or again the data may be the mortality from some disease with and without the administration of, say, a new antitoxin, the statistics giving

number who died to whom antitoxin was administered,

„ „ to whom antitoxin was not administered;

* To distinguish it from the “correlation” of continuous variables.

number who did not die to whom antitoxin was not administered,
 „ „ „ to whom antitoxin was administered ;

and from these data a discussion of the value of the cure is required. Here there is no scale of "death" ; there may be a scale of "antitoxin" if the dose varied, but not otherwise.

§ 2. Evidently such cases are of great importance, but the theory and means of handling them have received little attention from statisticians. Logicians have had a monopoly of the theory, but the superior interests of pure logic seem generally to have hindered them from developing it in a practical direction. The classical writings on the subject are, I suppose, those of DE MORGAN,* BOOLE,† and JEVONS.‡ Without attempting to criticise the work of his predecessors, to both of whom he was of course greatly indebted, the method of the latter must be allowed to far exceed theirs in clearness and simplicity. BOOLE's calculus of elective operators is highly complex in its working and necessitates the remembrance of many somewhat artificial rules ; JEVONS' method is practically intuitive. It is a matter of surprise to me that JEVONS never made any practical application of his method (so far as I am aware) during the decade or more that elapsed between the publication of his paper (*loc. cit.*) and his death. The following is a brief explanation of his notation and method.

§ 3. The symbols A, B, C, &c., are used to denote objects or individuals having the qualities A, B, C, &c. The terms enclosed in brackets thus—(A), (B), (C), &c., denote the *frequency* of individuals possessed of the quality or qualities A, B, or C, or the total number of such individuals observed in the given "universe of discourse."§ A compound term like AB denotes the class or group possessed of both qualities A and B, and (AB) its frequency ; compound groups may occur with any number of specified qualities, *i.e.* (ABC), (ABCD), or (BDKMN). Corresponding to each positive term there is a negative term which we shall denote by a small Greek letter|| α , β , γ , &c. Thus α signifies "not A," β "not B," and so on ; and (α), (β), &c., their frequencies. All symbols are used non-exclusively, A signifying objects *having the quality A with or without others*, and so on, consequently the frequency of any class can be expanded in terms of the frequencies of its sub-classes.

* 'Formal Logic,' chap. VIII., "On the Numerically Definite Syllogism," 1847.

† 'Analysis of Logic,' 1847. 'Laws of Thought,' 1854.

‡ "On a General System of Numerically Definite Reasoning," 'Memoirs of Manchester Literary and Philosophical Society,' 1870. Reprinted in 'Pure Logic and other Minor Works,' Macmillan, 1890.

§ I have used this convenient term of the logicians for the "material discussed" throughout the paper. There seems no exact equivalent in ordinary statistical language.

|| I have substituted small Greek letters for JEVONS' italics. Italics are rather troublesome when reading, as one has to spell out a group like *AbcDE*, "big A, little *b*, little *c*, big D, big E." It is simpler to read $A\beta\gamma DE$. The Greek becomes more troublesome when many letters are wanted, owing to the non-correspondence of the alphabets, but this is not often of consequence.

Thus

$$\begin{aligned}
 (A) &= (AB) + (A\beta) \\
 &= (ABC) + (AB\gamma) + (A\beta C) + (A\beta\gamma) \\
 &= (ABCD) + (ABC\delta) + (AB\gamma D) + (A\beta\gamma\delta) \\
 &\quad + (A\beta CD) + (A\beta C\delta) + (A\beta\gamma D) + (A\beta\gamma\delta) \\
 &= \&c.
 \end{aligned}$$

and also if (U) be the total frequency (total number of observations, total number in the "universe of discourse")

$$(U) = (A) + (\alpha) = (B) + (\beta) = (C) + (\gamma) = \&c.$$

The whole of JEVONS' method, so far as applied to purely numerical problems, depends on the use of equations of the above form, or the expansion of groups in terms of their sub-classes.

§ 4. We shall adopt the following conventions. When requiring to distinguish the qualities denoted by English letters from those denoted by Greek, we shall call the former *positive* qualities, the latter *negative*. A group in which all the qualities specified are positive will be called a positive group, and conversely.

A group specified by n qualities (positive or negative) will be termed an n th order group.

To distinguish the n th order groups in n variables from n th order groups formed from a larger number of variables, we shall refer to the former as "ultimate" groups.

Two groups such that each quality in the one is the negative (or *contrary*) of each quality in the other will be termed contrary groups, and their frequencies contrary frequencies. Thus

ABCD	$\alpha\beta\gamma\delta$
αBC	$A\beta\gamma$
$\alpha\beta\gamma DE$	$ABC\delta\epsilon$

are pairs of contraries. The case where the frequencies of contrary groups are equal is of some importance. This will be called the case of "equality of contraries."

Consider, for example, the case of normally correlated continuous variables. If A denote the class in which some quality is above the average, α the class in which the same is below* average, and so on with B , β , &c., then from the symmetry of the surface we must have

* Logically "not above average"; but we take the average as a mathematical point, so that there are no individuals with exactly average qualities.

$$\begin{aligned}
(A) &= (a) \\
(B) &= (\beta), \quad \&c., \\
(AB) &= (a\beta) \\
(\alpha B) &= (A\beta), \quad \&c., \\
(ABC) &= (\alpha\beta\gamma) \\
(AB\gamma) &= (\alpha\beta C), \quad \&c.,
\end{aligned}$$

and so on with groups of any order.

I shall return later to this case and to the properties that this equality of contraries produces.

§ 5. It may be noted at this point that groups may often be rapidly expanded by using ABC, &c., as "elective operators" in BOOLE'S sense, and using the general law of multiplication of operators, with the special conditions

$$UA = A,$$

i.e., selecting out the universe of discourse, and then selecting out the A's from it, is the same thing as selecting out the A's at once, and the "index law"

$$A^* = A,$$

i.e., repeating the operation of selecting out the A's has no effect on the objects included.

To denote that the letters are being used as operators we will use square brackets. Thus

$$\begin{aligned}
[AB\gamma] &= [U - \alpha][U - \beta][U - C] \\
&= [U^3] - [U^2\alpha] - [U^2\beta] - [U^2C] + [U\alpha\beta] + [U\alpha C] + [U\beta C] - [\alpha\beta C]
\end{aligned}$$

or

$$(AB\gamma) = (U) - (\alpha) - (\beta) - (C) + (\alpha\beta) + (\alpha C) + (\beta C) - (\alpha\beta C).$$

We only mention the process as it affords such a rapid and easy means of expansion. The results obtained by its use can always be obtained at a little greater length by an elementary process of step-by-step substitution.

§ 6. Before proceeding to the consideration of association and so forth, it seems necessary to discuss somewhat fully the general relations subsisting between the frequencies of different groups, and the number of *independent* frequencies of any order. Suppose, for example, we are dealing with three attributes (A, B, C and their contraries). Twelve second order and eight third order groups can be formed from these. It might appear then that if the frequencies of the second order groups were given, there would be a sufficient number of equations to determine the frequencies of the third order groups. As a matter of fact this is not so; the twelve second order frequencies do not form independent data, and the question arises, How many are independent? or, in general, how many independent frequencies or groups are there in the *m*th order groups produced from *n* variables? *i.e.*, how many of these

m th order frequencies must be given (nothing else being given) in order that the remaining frequencies of the same order may be calculated? These questions are considered in the next section (II.). In Section III. correlation or *association* and its measurement are treated; Section IV. deals with probable errors; and in Section V. some arithmetical examples are given of the methods and results previously discussed.

II.—GENERAL RELATIONS.

Number of Independent Frequencies.

§ 7. Before proceeding to the problem above described, we will first prove the theorem—

“The frequency of any group whatever can always be expressed entirely in terms of the frequencies of the *positive* groups of its own and lower orders, and the total frequency (U).”

This theorem may most simply be proved by the method of multiplying operators as described in the introduction, replacing any negative operator like α by A and multiplying out. We may, however, effect the reduction by step-by-step substitution. Thus

$$\begin{aligned}(A\beta\gamma) &= (A\beta) - (A\beta C) \\ &= (A) - (AB) - (AC) + (ABC).\end{aligned}$$

To take terms of the fourth order, for instance—

$$\begin{aligned}(ABCD) &= (ABCD) \\ (ABC\delta) &= (ABC) - (ABCD) \\ (AB\gamma\delta) &= (AB) - (ABC) - (ABD) + (ABCD) \\ (A\beta\gamma\delta) &= (A) - (AB) - (AC) - (AD) + (ABC) + (ABD) + (ACD) - (ABCD) \\ (\alpha\beta\gamma\delta) &= (U) - (A) - (B) - (C) - (D) + (AB) + (AC) + (AD) + (BC) \\ &\quad + (BD) + (CD) - (ABC) - (ABD) - (ACD) - (BCD) + (ABCD) \\ &\quad \dots \dots (1).\end{aligned}$$

Evidently from the form of the last equation *all* the positive groups are required to express the frequency of an entirely negative group.

§ 8. Now to the problem—

“To find the number of independent frequencies of m th order groups, the number of variables being n .”

The number of *positive* groups of order m is (number of combinations of n things m together)

$$\frac{n(n-1) \dots (n-m+1)}{m!}.$$

But by the theorem of § 7 the frequency of any group of the m th order can be expressed entirely in terms of the frequencies of positive groups. Therefore the number of *independent* m th order frequencies must be equal simply to the total

number of positive groups of the m th and lower orders, including (U), the group of order zero; that is, equal to

$$1 + n + \frac{n(n-1)}{1 \cdot 2} + \dots + \frac{n(n-1) \dots (n-m+1)}{m!}$$

or

“The number of independent frequencies of the m th order in n variables is equal to the sum of the first $(m+1)$ binomial coefficients.”

This gives the following expressions for the number of independent frequencies of the second, third, fourth, and fifth orders—

$$\begin{aligned} \text{Order 2nd} & \dots \dots \dots \frac{1}{2}(n^2 + n + 2) \\ \text{,, 3rd} & \dots \dots \dots \frac{1}{6}(n^3 + 5n + 6) \\ \text{,, 4th} & \dots \dots \dots \frac{1}{24}(n^4 - 2n^3 + 11n^2 + 14n + 24) \\ \text{,, 5th} & \dots \dots \dots \frac{1}{120}(n^5 - 5n^4 + 25n^3 + 5n^2 + 94n + 120). \end{aligned}$$

The *total* number of frequencies of any order m is equal to the number of positive frequencies of that order (see above) multiplied by 2^m , since each letter, A, B, &c., may be replaced by its negative, and this gives the following expressions for the second to fifth orders:—

$$\begin{aligned} \text{Order 2nd} & \dots \dots \dots 2n(n-1) \\ \text{,, 3rd} & \dots \dots \dots \frac{4}{3}n(n-1)(n-2) \\ \text{,, 4th} & \dots \dots \dots \frac{2}{3}n(n-1)(n-2)(n-3) \\ \text{,, 5th} & \dots \dots \dots \frac{4}{15}n(n-1)(n-2)(n-3)(n-4). \end{aligned}$$

It is evident from these expressions that, in the general case, the frequencies of any order can never be expressed in terms of lower order frequencies.

Table I. below gives the number of independent frequencies and the total number from $n = 2$ to $n = 6$ and $m = 2$ to $m = 6$.

TABLE I.

Number of Groups of the										
Number of variables. n .	2nd order.		3rd order.		4th order.		5th order.		6th order.	
	Inde- pendent.	Total.	Inde- pendent.	Total.	Inde- pendent.	Total.	Inde- pendent.	Total.	Inde- pendent.	Total.
2	4	4	—	—	—	—	—	—	—	—
3	7	12	8	8	—	—	—	—	—	—
4	11	24	15	32	16	16	—	—	—	—
5	16	40	26	80	31	80	32	32	—	—
6	22	60	42	160	57	240	63	192	64	64

§ 9. *Case of Equality of Contraries.*

Before proceeding to the determination of the numbers of independent frequencies in this case, we shall first prove the following three theorems:—

Theorem I. If equality of contraries subsist for frequencies of any given order, then it subsists for all lower orders.

Theorem II. If equality of contraries subsist for any even order of frequencies, say $2m$, then it need not in general subsist for order $2m + 1$. If, however, it be assumed to subsist for order $2m + 1$, then the frequencies of this order can be expressed in terms of those of the lower order $2m$.

Theorem III. If equality of contraries subsist for any odd order of frequencies, say $2m - 1$, then it must subsist also in frequencies of the next higher order $2m$. But frequencies of this higher order cannot be expressed in terms of those of order $2m - 1$.

The first theorem may be very simply proved.

§ 10. Suppose we are given, for example, that equality of contraries subsists for frequencies of the fifth order; then we have

$$\begin{aligned}(ABCDE) &= (a\beta\gamma\delta\epsilon) \\ (ABCD\epsilon) &= (a\beta\gamma\delta E)\end{aligned}$$

or adding

$$(ABCD) = (a\beta\gamma\delta)$$

and so on. The expansions of contrary frequencies are in fact necessarily contrary themselves.

§ 11. Next for Theorem II. To take the simplest case, let us suppose equality of contraries given for the second order frequencies. Take any third order group and expand it in terms of its contrary and second order frequencies. This may be done most elementarily step by step. Thus

$$\begin{aligned}(aBC) &= (BC) - (ABC) \\ \therefore (a\beta C) &= (aC) - (BC) + (ABC) \\ \therefore (a\beta\gamma) &= (a\beta) - (aC) + (BC) - (ABC).\end{aligned}$$

Evidently no equality of contraries amongst second order groups will give us $(a\beta\gamma) = (ABC)$. But if we assume this relation to hold we must have

$$\left. \begin{aligned}2(ABC) &= (a\beta) - (aC) + (BC) \\ &= (AB) + (BC) - (aC)\end{aligned} \right\} \dots \dots \dots (2),$$

an equation which expresses the third order frequencies in terms of the second. Similarly if equality of contraries is to subsist amongst fifth order groups when it subsists amongst those of the fourth order, we must have

$$2(ABCDE) = (ABCD) + (BCDE) + (AB\delta\epsilon) - (ABC\epsilon) - (aCDE). \dots (3).$$

As the method of expansion used is evidently quite general, this proves Theorem II.

Equations (2) and (3) are evidently quite special relations. The set of arbitrary frequencies in Table II. below is drawn up to illustrate the theorem for the case of

TABLE II.

1. Group.	2. Frequency.	3. Group.	4. Frequency.	5. Group.	6. Frequency.	7. Frequency.
A . .	91	AB . .	27	ABC . . .	18	15
B . .	91	BC . .	59	α BC . . .	41	44
C . .	91	AC . .	41	$\Lambda\beta$ C . . .	23	26
α . .	91	$\Lambda\beta$. .	64	$\Lambda B\gamma$. . .	9	12
β . .	91	$\Lambda\gamma$. .	50	$\alpha\beta$ C . . .	9	6
γ . .	91	B γ . .	32	$\alpha B\gamma$. . .	23	20
		αB . .	64	$\Lambda\beta\gamma$. . .	41	38
		αC . .	50	$\alpha\beta\gamma$. . .	18	21
		βC . .	32			
		$\alpha\beta$. .	27			
		$\beta\gamma$. .	59			
		$\alpha\gamma$. .	41			

second and third order frequencies. Column 4 gives a set of second order frequencies for which equality of contraries subsists, the numbers for this having been in other respects written down at random. These give the first order frequencies of Column 2. If we now proceed to calculate the third order frequencies by equations of the above form,

$$2(ABC) = (AB) + (BC) - (\alpha C),$$

that is, using the figures of Column 4,

$$2(ABC) = 27 + 59 - 50$$

$$= 36$$

$$(ABC) = 18,$$

we get a set of frequencies, Column 6, for which equality of contraries subsists.

If we take, however, an arbitrary value for (ABC), say 15, and calculate the remaining frequencies of the same order from it, we get a set of third order frequencies (Column 7 of Table II.) for which equality of contraries does not subsist, but which is equally consistent with the second order frequencies.

§ 12. Now apply precisely the same method to a group of the fourth order. We get finally

$$(\alpha\beta\gamma\delta) = (\alpha\beta\gamma) - (\alpha\beta\delta) + (\alpha\delta\gamma) - (\beta\delta\gamma) + (\alpha\beta\delta\gamma).$$

But if equality of contraries subsist for the third order groups, we have by the theorems of § 11, § 10—

$$\begin{aligned} 2\{(\alpha\beta\gamma) + (\alpha\delta\gamma)\} &= (\alpha\beta) + (\beta\gamma) - (\Lambda\gamma) + (\alpha C) + (CD) - (AD) \\ &= (\alpha\beta) + (\beta\gamma) + (CD) - (AD) \end{aligned}$$

$$\begin{aligned}
 2 \{(\alpha\beta D) + (BCD)\} &= (\alpha\beta) + (\beta D) - (AD) + (BC) + (CD) - (\beta D) \\
 &= (\alpha\beta) + (BC) + (CD) - (AD) \\
 &= 2 \{(\alpha\beta\gamma) + (\alpha CD)\} \\
 \therefore (\alpha\beta\gamma\delta) &= (ABCD)
 \end{aligned}$$

i.e., if contrary frequencies are equal in the case of third order groups they are equal in the case of fourth order groups.

The method of proof is again quite general in its application, so Theorem III. is proved.

I have thought it again worth while to illustrate the theorem numerically, and have drawn up Table III. for the purpose. A set of arbitrary fourth order frequencies (set (1)), with contraries equal, was first written down, and from them the given set

TABLE III.

	(1).	(2).	(3).		
ABCD . . .	34	30	11	ABC and $\alpha\beta\gamma$. . .	58
ABC δ . . .	24	28	47	ABD " $\alpha\beta\delta$. . .	91
AB γ D . . .	57	61	80	ACD " $\alpha\gamma\delta$. . .	102
A β CD . . .	68	72	91	BCD " $\beta\gamma\delta$. . .	76
α BCD . . .	42	46	65	α BC " $\alpha\beta\gamma$. . .	79
AB $\gamma\delta$. . .	29	25	6	A β C " $\alpha B\gamma$. . .	107
A β C δ . . .	39	35	16	AB γ " $\alpha\beta C$. . .	86
α BC δ . . .	37	33	14	α BD " $\alpha\beta\delta$. . .	81
A $\beta\gamma$ D . . .	37	33	14	A β D " $\alpha B\delta$. . .	105
$\alpha B\gamma$ D . . .	39	35	16	AB δ " $\alpha\beta D$. . .	53
$\alpha\beta$ CD . . .	29	25	6	α CD " $\alpha\gamma\delta$. . .	71
A $\beta\gamma\delta$. . .	42	46	65	$\alpha\gamma$ D " $\alpha C\delta$. . .	94
$\alpha B\gamma\delta$. . .	68	72	91	AC δ " $\alpha\gamma D$. . .	63
$\alpha\beta C\delta$. . .	57	61	80	β CD " $B\gamma\delta$. . .	97
$\alpha\beta\gamma$ D . . .	24	28	47	B γ D " $\beta C\delta$. . .	96
$\alpha\beta\gamma\delta$. . .	34	30	11	BC δ " $\beta\gamma D$. . .	61
	660	660	660		

of third order frequencies calculated. Now our theorem tells us that the equality amongst the fourth orders depends solely on equality amongst the thirds; so that we ought to be able to get any number of sets of fourth order frequencies, *all* possessing equality of contraries, and *all* consistent with the given set of third order. That this is so will be at once evident on trial. Take

$$(ABCD) = 30$$

for instance. Then we have at once

$$(ABC\delta) = (ABC) - (ABCD) = 58 - 30 = 28$$

$$(AB\gamma\delta) = (AB\delta) - (ABC\delta) = 53 - 28 = 25$$

$$(A\beta\gamma\delta) = (A\gamma\delta) - (AB\gamma\delta) = 71 - 25 = 46$$

$$(\alpha\beta\gamma\delta) = (\beta\gamma\delta) - (A\beta\gamma\delta) = 76 - 46 = 30$$

giving

$$(ABCD) = (\alpha\beta\gamma\delta) = 30.$$

Similarly all the other frequencies may be calculated, and we get set (2).

If we take $(ABCD) = 11$ we get set (3). All three sets are consistent with the set of third order, and possess equality of contraries. The state of affairs is precisely the opposite of that illustrated by Table II., where only *one* set of third order frequencies could be obtained, consistent with the given set of the second order, and possessing equality of contraries.*

It should be noted, however, that the possible number of fourth order sets in such a case as the present is not infinite, for certain limits are imposed by the fact that negative frequencies are impossible. Thus, if we take

$$(ABCD) = 60$$

we have

$$(ABC\delta) = 58 - 60 = -2$$

or if

$$(ABCD) = 3$$

$$(ABC\delta) = 58 - 3 = 55$$

$$(AB\gamma\delta) = 53 - 55 = -2,$$

so $(ABCD)$ must lie at all events between the limits 58 and 5.

§ 13. It follows from what we have proved that a state of *complete equality of contraries*, in which this state subsists for groups of all orders, is not and cannot be an artificial state created by choice of the points of division between A and α , B and β , and so on, but must arise from some real and natural symmetry in the distribution of frequency. In dealing then with the next problem, to find the number of independent frequencies of any order in the case of *complete* equality of contraries, we must not rashly apply the formulæ obtained (by extrapolation, as it were) to an empirical case in which we only know that the condition subsists for a few low orders.

The general result we arrived at was that the number of independent frequencies of the m th order in n variables was given by the sum of the first $(m + 1)$ terms of the series

$$1 + n + \frac{n(n-1)}{1 \cdot 2} + \frac{n(n-1)(n-2)}{1 \cdot 2 \cdot 3} + \dots$$

In this expression we may now strike out alternate terms commencing with n , for these represent frequencies of odd order which can be expressed in terms of the next lower order of frequencies, and so do not give any independent data. This leaves the series

$$1 + \frac{n(n-1)}{1 \cdot 2} + \frac{n(n-1)(n-2)(n-3)}{1 \cdot 2 \cdot 3 \cdot 4} + \dots$$

* Note 4 4/00.—I only noticed in reading Tables II. and III. in proof that the theorem holds "If two sets of ultimate m th order frequencies are both consistent with a given set of $m-1$ th order, the differences between corresponding pairs of m th order frequencies are numerically constant." It is noted below (pp. 272, 273) that this holds for second order frequencies. The theorem is proved at once by expanding the $(m-1)$ th order frequencies in terms of the two sets of the m th order.

and the number of independent frequencies of order $2m$ in n variables is equal to the sum of the first $m + 1$ terms of this series.

The number of independent frequencies of order $2m + 1$ is of course equal to the number of independent frequencies of order $2m$.

These rules give the numbers in Table IV. below.

TABLE IV.—Complete Equality of Contraries.

Number of variables.	Number of independent frequencies of order,				
	2	3	4	5	6
2	2				
3	4	4			
4	7	7	8		
5	11	11	16	16	
6	16	16	31	31	32

§ 14. In the 'Phil. Trans.' for 1898 a very striking theorem was given by Mr. W. F. SHEPPARD,* expressing the frequencies like (AB) , $(A\beta)$, &c., in quadrants of the normal surface in terms of the coefficient of correlation r . Our equations like (2) in § 11, on p. 263 above, enable us at once to extend the use of this theorem to the case of three variables. Let us take two examples from the case of Heredity on the assumption of Galton's Law.

(1) If the father and grandfather of a man are both above the average as regards any one character, what is the chance that he will be above the average?

The following are the correlation coefficients:—

Son and father	+ '3000
Son and grandfather	+ '1500
Father and grandfather	+ '3000

Mr. SHEPPARD's theorem then gives the following for the frequencies per 10,000 above and below average. —

		Son.	
		above	below
Father.	above	2985	2015
	below	2015	2985

		Son.	
		above	below
Grandfather.	above	2740	2260
	below	2260	2740

The first scheme holding for father and grandfather as well as son and father.

* 'Phil. Trans.' A, vol. 192, p. 101.

Now if we use ABC for son, father, grandfather, and the capitals to denote "above average," Greek letters "below average," we want

$$(ABC)/(BC)$$

(BC) = 2985 at once. From § 11, p. 263,

$$\begin{aligned} 2(ABC) &= (AB) + (BC) - (aC) \\ &= 2985 + 2985 - 2260 \\ &= 3710 \\ (ABC) &= 1855, \end{aligned}$$

chance required = $1855/2985 = \cdot 6214$.

If *only* the father be known to be above average, chance of son being above average = $2985/5000 = \cdot 5970$.

If, on the other hand, we ask what is the chance that the child will be above average if both the father and mother are so, we have, assuming the correlation with both parents to be the same, using B for father, C for mother, and assuming no assortative mating :—

$$\begin{aligned} 2(ABC) &= 2985 + 2500 - 2015 = 3470 \\ (ABC) &= (1735) \end{aligned}$$

chance = $1735/2500 = \cdot 6940$.

But if there be *perfect* assortative mating

$$\begin{aligned} 2(ABC) &= 2985 + 5000 - 2015 \\ &= 5970 \quad (ABC) = 2985 \end{aligned}$$

chance = $2985/5000 = \cdot 5970$.

Thus, if there be no assortative mating, a selection of father and mother is better than a selection of parent and grandparent ; but not so if there be assortative mating to any great extent.

§ 15. The relations that we have dealt with in the preceding pages have a general bearing on the theory of certain multiple integrals. If we imagine, as we have already done on several occasions, that the distribution of frequency is really continuous and the points of division between A and α , B and β , &c., arbitrarily fixed, then any ultimate frequency like (ABCD) ($A\beta C\delta$), for example, is equivalent to the multiple integral expressing the total frequency contained within the four axes of the frequency surface (or hyper-surface), taking each of these axes in either the positive or negative direction.

Now we know that there are 2^n ultimate groups (or multiple integrals of the above kind) to be formed from n variables, all of these groups being in the general case independent. Suppose the function expressing the distribution of frequency to contain m constants that remain in the expression, $\phi(a_1, a_2, a_3, \dots, a_m)$, for the multiple integral. Then we have the equations

$$\begin{aligned}
 (ABCD \dots) &= \phi_1(a_1, a_2, a_3, \dots a_m) \\
 (\alpha BCD \dots) &= \phi_2(a_1, a_2, a_3, \dots a_m) \\
 &\quad \&c. \qquad \&c.
 \end{aligned}$$

or 2^n equations altogether. But if $m < 2^n$, we can express the constants in terms of the frequencies by means of the first m equations, and then insert their values in the remaining equations, thus obtaining $2^n - m$ necessary relations between the frequencies. If the surface we are dealing with is symmetrical, there will be only 2^{n-1} independent ultimate groups, and m must be less than 2^{n-1} if special relations are to subsist between the groups.

Now this is the case in the normal surface itself. The standard deviations will not appear in any of the multiple integrals, which must be functions solely of the correlation coefficients, r_{12} , r_{13} , r_{23} , &c., and the total frequency. That is to say n variables give $1 + \frac{n(n-1)}{2}$ constants that appear in the expressions for the total frequencies of the ultimate groups. This gives the following figures:—

n	$1 + \frac{n(n-1)}{2}$	2^{n-1}
2	2	2
3	4	4
4	7	8
5	11	16
6	16	32

There must therefore be one relation subsisting between the ultimate fourth order groups in normal correlation—besides the mere equality of contrary frequencies—five relations between the fifth order groups, sixteen between those of the sixth order, and so on. If we could find these relations the expression of fourth order frequencies in terms of third, sixth in terms of fifth, and so on, would cease to be indeterminate as in the general case of equality of contraries. Mr. SHEPPARD'S theorem could then be extended to the case of groups of any order in normal correlation, which would give results of great interest for calculating certain chances, *e.g.*, the chance of a man being above average when his father, father and grandfather, father, grandfather, and great-grandfather were above average.

Finding myself quite unable to solve the above problem, I have handed it to Professor KARL PEARSON; he informs me that the relations sought depend on equations between the area, sides, and angles of the generalised spherical triangle in hyper-space, but the problem has not yet been solved. It is curious that investigations into the theory of logic should lead to properties of hyper-spherical triangles or tetrahedra.

III. ASSOCIATION.

§ 16. Two qualities or attributes, A and B, are defined to be independent if the chance of finding them together is the product of the chances of finding either of them separately, *i.e.*, if

$$\frac{(AB)}{(U)} = \frac{(A)}{(U)} \cdot \frac{(B)}{(U)},$$

or

$$(AB)(U) = (A)(B).$$

This is, I think, the only legitimate test of dependence or independence—association or non-association—in the general case.

§ 17. *Theorem.*—To show that if

$$(AB)(U) = (A)(B)$$

then

$$(A\beta)(U) = (A)(\beta)$$

$$(aB)(U) = (a)(B)$$

$$(a\beta)(U) = (a)(\beta).$$

Take the first equation of these three—

$$\begin{aligned} (A)(\beta) &= (A) \{(U) - (B)\} = (U)(A) - (AB)(U) \\ &= (A\beta)(U), \end{aligned}$$

and so on for the others. So that if the chance of finding the two qualities together is the product of the chances of finding either of them separately, the chance of finding the one without the other is the chance of finding the one multiplied by the chance of not finding the other, and so on. Any one of the relations implies all the others.

§ 18. It follows at once from the above that if two attributes (A) and (B) are independent, the products of the contrary second order frequencies are equal, *i.e.*,

$$(AB)(a\beta) = (A\beta)(aB),$$

for each is equal to (A)(B)(a)(β) divided by (U)². Not only so, but the converse is also true—

§ 19. *If the cross-products are equal the variables are independent.* Thus let

$$(AB)(a\beta) = (A\beta)(aB).$$

Now

$$(A\beta) = (A) - (AB)$$

$$(aB) = (B) - (AB)$$

$$(a\beta) = (\beta) - (A\beta)$$

$$= (\beta) - (A) + (AB).$$

Therefore

$$\begin{aligned}(AB) \{(\beta) - (A) + (AB)\} &= \{(A) - (AB)\} \{(B) - (AB)\} \\(AB) \{(\beta) - (A)\} &= (A)(B) - (AB) \{(A) + (B)\} \\(AB) \{(B) + (\beta)\} &= (A)(B) \\(AB)(U) &= (A)(B).\end{aligned}$$

§ 20.* Now it seems to me that one of the chief needs in handling statistics of the kind we are considering is some sort of "coefficient of association," which should take the place of the "*coefficient of correlation*" for continuous variables, and be a measure of the approach of association towards complete independence on the one hand and complete association on the other. Such a coefficient should —

(1) Be zero when the variables or attributes A, B, are independent, and only when they are independent.

(2) It should be +1 when, and only when, A and B are completely associated, i.e., when either

all A's are B }
all β 's are α }

or

all B's are A }
all α 's are β }

or when both of these statements are true together, which can only be when

$$(A) = (B), \quad (\alpha) = (\beta).$$

The three diagrams below illustrate the three cases which correspond to

$$(A\beta) = 0, \quad (\alpha B) = 0, \quad (A\beta) = (\alpha B) = 0.$$

	(B)	(β)
(A)	(AB)	0
(α)	(αB)	($\alpha\beta$)

	(B)	(β)
(A)	(AB)	(A β)
(α)	0	($\alpha\beta$)

	(B)	(β)
(A)	(AB)	0
(α)	0	($\alpha\beta$)

(3) It should be -1 when, and only when, A and β or B and α are completely associated, i.e., when either

all A's are β }
all B's are α }
all β 's are A }
all α 's are B }

* Note added 19/1/00.—It has several times occurred to me as quite possible that I have limited myself too much in this section by defining the case of "complete association" as equivalent simply to the logical case. An association coefficient of greater analytical convenience might have been obtained by defining attributes A and B as completely associated only when all A's were B and all B's were A. The distinction of the logical case by a definite value of the association has, however, obvious conveniences.

or when both of these statements are true, which again can only be if

$$A = (a) \quad (B) = (\beta).$$

The three diagrams below illustrate these cases of negative association which correspond to

$$(AB) = 0 \quad , \quad (a\beta) = 0 \quad , \quad (AB) = (a\beta) = 0.$$

	B	β
A	0	$A\beta$
a	aB	$a\beta$

	B	β
A	AB	$A\beta$
a	aB	0

	B	β
A	0	$A\beta$
a	aB	0

§ 21. The theorems just given show that

$$Q = \frac{(AB)(a\beta) - (A\beta)(aB)}{(AB)(a\beta) + (A\beta)(aB)} \quad \dots \quad (i)$$

will serve as such a coefficient of association for--

(1) When A and B are independent the numerator is zero and therefore Q zero; and conversely when Q is zero the variables are independent.

(2) When $(A\beta) = 0$ or $(aB) = 0$, or both, $Q = +1$; and conversely when $Q = +1$ $(A\beta) = 0$, $(aB) = 0$, or both.

(3) When $(A\beta) = 0$ or $(aB) = 0$, or both, $Q = -1$; and conversely when $Q = -1$ $(AB) = 0$ or $(a\beta) = 0$, or both.

It is perfectly possible that other simple functions of the frequencies might be devised which should have the same properties, but Q at any rate will serve; I do not wish to attach too great importance to the identical function employed. If we choose Q for such a purpose, however, its properties must be investigated.

§ 22. The numerator, or difference of the cross-products, has, as Professor KARL PEARSON has pointed out to me, a very simple and important physical meaning. It follows immediately from the equations used in § 19 for showing that when the cross-products were equal A and B were independent; namely--

$$(AB)(a\beta) - (A\beta)(aB) = (AB)(U) - (A)(B);$$

or if $(AB)_0$ be the value (AB) would have if Q were zero

$$\begin{aligned} (AB)(a\beta) - (A\beta)(aB) &= (U) \{ (AB) - (AB)_0 \} \\ &= (U) \{ (a\beta) - (a\beta)_0 \} \\ &= (U) \{ (A\beta)_0 - (A\beta) \} \\ &= (U) \{ (aB)_0 - (aB) \} \end{aligned}$$

That is to say, "The excesses of (AB) and $(\alpha\beta)$ above $(AB)_0$ and $(\alpha\beta)_0$, and of $(A\beta)_0$ and $(\alpha B)_0$ above $(A\beta)$ and (αB) , are all equal, and equal to the ratio of the difference of the cross-products to the number of observations." This theorem seems to me rather remarkable. I can find no similar relation for the sum of the cross-products so as to give a complete physical meaning to Q .

§ 23. Next let us determine any one of the second order frequencies, *e.g.* (AB) , in terms of Q and the first order frequencies.

If we write

$$\kappa = \frac{1 - Q}{1 + Q} \quad (2)$$

we have

$$\kappa (AB) (\alpha\beta) = (\alpha B) (A\beta) \quad (3).$$

Now

$$\begin{aligned} (\alpha B) &= (B) - (AB) \\ (A\beta) &= (A) - (AB) \\ (\alpha\beta) &= (\beta) - (A) + (AB), \end{aligned}$$

whence

$$(AB)^2 (1 - \kappa) - (AB) \{ \kappa (U) + (1 - \kappa) [(A) + (B)] \} + (A)(B) = 0$$

which is a quadratic for (AB) .

Now let

$$\left. \begin{aligned} \frac{(A) - (\alpha)}{(A) + (\alpha)} &= s_1 \\ \frac{(B) - (\beta)}{(B) + (\beta)} &= s_2 \end{aligned} \right\} \quad (4),$$

where s_1, s_2 may be called the surpluses of A and B . It follows that

$$\left. \begin{aligned} (A) &= \frac{1}{2} (U) (1 + s_1) \\ (\alpha) &= \frac{1}{2} (U) (1 - s_1) \end{aligned} \right\} \quad (5)$$

and similarly for (B) and (β) . In terms of these symbols the quadratic may be written

$$(AB)^2 - (AB)(U) \frac{2 + (1 - \kappa)(s_1 + s_2)}{2(1 - \kappa)} + \frac{(U)^2}{4} \frac{(1 + s_1)(1 + s_2)}{(1 - \kappa)} = 0$$

whence

$$(AB) = \frac{(U)}{4(1 - \kappa)} \left\{ 2 + (1 - \kappa)(s_1 + s_2) \pm \sqrt{(s_1 - s_2)^2 + \kappa[4 - (s_1 - s_2)^2 - (s_1 + s_2)^2] + \kappa^2(s_1 + s_2)^2} \right\} \quad (6),$$

or replacing κ by the original Q ,

$$(AB) = \frac{(U)}{4Q} \left\{ 1 + Q(1 + s_1 + s_2) \pm \sqrt{1 - 2Qs_1s_2 - Q^2(1 - s_1^2 - s_2^2)} \right\} \quad (7).$$

§ 24. The question arises, what is the meaning of the alternative sign in the expression for (AB) ? One of the values given is, as a matter of fact, only a numerical solution, and is really impossible, so that the value of (AB) is not indeterminate. We may write (7) in the form

$$\frac{(AB)}{(A)} = \frac{1}{2Q(1 + s_1)} \left\{ 1 + Q(1 + s_1 + s_2) \pm \sqrt{1 - 2Qs_1s_2 - Q^2(1 - s_1^2 - s_2^2)} \right\} \quad (8),$$

and $\frac{(AB)}{(A)}$ must be less than 1 and greater than 0.

The product of the two values given by the $+$ and $-$ sign is

$$\frac{(1 + Q)(1 + s_2)}{2Q(1 + s_1)}.$$

If Q be negative this is negative, and so the lower value is negative or impossible; we must consequently use the $+$ sign. On the other hand, if we subtract 1 from each value above and again form the product, it is

$$\frac{(Q - 1)(1 - s_2)}{2Q(1 + s_1)},$$

and this is negative if Q be positive; hence *one* of the values is greater than unity. When Q is positive we must therefore use the $-$ sign to the radical.

If $Q = +1$, one of the roots is unity and the other greater or less, according as $s_2 \geq s_1$. Thus, if $Q = +1$ we have for (AB)

$$(AB) = \frac{(U)}{2}(1 + s_1) \quad \text{or} \quad \frac{(U)}{2}(1 + s_2),$$

i.e.,

$$(AB) = (A) \quad \text{or} \quad (B).$$

If Q is -1 on the other hand, one root is zero

$$(AB) = 0 \quad \text{or} \quad \frac{(U)}{2}(s_1 + s_2).$$

§ 25. The values of all four groups are as follows. the first sign of the radical to be used when Q is positive :—

$$(AB) = \frac{(U)}{4Q} \left\{ 1 + Q(1 + s_1 + s_2) \mp \sqrt{1 - 2Qs_1s_2 - Q^2(1 - s_1^2 - s_2^2)} \right\}$$

$$(A\beta) = \frac{(U)}{4Q} \left\{ -1 + Q(1 + s_1 - s_2) \pm \sqrt{} \right\}$$

$$(\alpha B) = \frac{(U)}{4Q} \left\{ -1 + Q(1 + s_2 - s_1) \pm \sqrt{\dots} \right\}$$

$$(\alpha \beta) = \frac{(U)}{4Q} \left\{ 1 + Q(1 - s_1 - s_2) \mp \sqrt{\dots} \right\}$$

If $s_1 = s_2 = 0$, *i.e.*, if equality of contraries subsist amongst the first and second order groups, we have

$$\begin{aligned} (AB) &= \frac{(U)}{4Q} \{1 + Q \pm \sqrt{1 - Q^2}\} \dots \dots \dots (9). \\ &= \frac{(U)}{2} \cdot \frac{1}{1 + \sqrt{\kappa}} \end{aligned}$$

The following short table gives the values of κ and $\sqrt{\kappa}$ for different values of Q . The values of κ and $\sqrt{\kappa}$ corresponding to negative Q 's are the reciprocals of those corresponding to the positive values :—

Q.	κ .	$\sqrt{\kappa}$.
0	1	1
+ { .1	.8182	.9045
.2	.6667	.8165
.3	.5385	.7338
.4	.4286	.6547
.5	.3333	.5773
.6	.2500	.5000
.7	.1765	.4201
.8	.1111	.3333
.9	.0526	.2294
1.0	0	0
- { .1	1.2222	1.1056
.2	1.5000	1.2247
.3	1.8570	1.3628
.4	2.3333	1.5274
.5	3.0000	1.7321
.6	4.0000	2.0000
.7	5.6667	2.3804
.8	9.0000	3.0000
.9	19.0000	4.3589
1.0	∞	∞

Association and Correlation.

§ 26. The theorem already referred to, due to Mr. W. F. SHEPPARD,* forms a connecting link between BRAVAIS' coefficient of correlation and the association coefficient in the case of normal correlation. If the divisions between A and α , B and β , &c., are the means of the corresponding variables

* 'Phil. Trans.,' A, 1898, vol. 162, p. 101.

$$\left. \begin{aligned} r &= -\cos \frac{(AB)}{(A)} \pi = \cos \frac{(A\beta)}{(A)} \pi \\ &= \cos \frac{\sqrt{\kappa}}{1 + \sqrt{\kappa}} \pi \end{aligned} \right\} \dots \dots \dots (10)$$

where

$$\kappa = \frac{1 - Q}{1 + Q} \text{ as before.}$$

The figures below give corresponding values of Q and r :—

Q .	r .	Q .	r .
0	0	·6	·500
·1	·079	·7	·598
·2	·158	·8	·707
·3	·239	·9	·833
·4	·322	1·0	1·000
·5	·409		

Q is always slightly in excess of r , the greatest difference being rather more than ·1 for $Q = \cdot 7$.

§ 27. In the general case the value of Q is necessarily a function of the position of the origin, or of the arbitrary axes which are chosen for dividing A from α and B from β . The evaluation of Q for any pair of axes in the case of normal correlation, depends on that of certain definite integrals which have not yet been tabulated. To get some idea of the general character of the dependence I have calculated the value of Q for every possible pair of axes in the annexed (observed) frequency table; the frequencies* being the small figures, and the values of Q those entered in heavy type at each origin. An inspection of the table will show that Q is a minimum for axes near the mean of the whole table, and a maximum for origins near the limits. At the extreme boundary the values vary suddenly and erratically, owing to the necessary discontinuity of the observed frequencies, and here we may get values ± 1 for the association. In other parts of the table, however, negative values only occur in most exceptional positions, and appear to be due to accidental irregularities. The sign of Q agrees with that of the correlation coefficient r over almost the whole table.

§ 28. It does not seem possible to obtain for Q a function that shall not vary with the position of the axes in the general case, so long, at all events, as we adhere to certain conditions of symmetry for the function Q that seem to me almost necessary. It may perhaps be possible for a strictly normal frequency distribution.

* There is some slight error, possibly due to copying, in the frequencies of the table, as the totals of rows and columns occasionally contain odd quarters, whereas they should only contain odd halves. I do not think this is of any practical consequence.

[illegible]

There is one case, and one only, where Q is independent of the axes chosen, and that is where the variables are strictly independent. Let f_m, f_n' be the elementary

	f_1'	f_2'	f_3'
f_1	F_{11}	F_{12}	F_{13}
f_2	F_{21}	F_{22}	F_{23}
f_3	F_{31}	F_{32}	F_{33}

frequencies corresponding to values x_m, y_n of the variables, and let F_{mn} be the frequency of the pair (x_m, y_n) . Then, if the variables are strictly independent, we must have in every case

$$N \cdot F_{m \cdot n} = f_m \times f_n'$$

N being the total number of observations. Therefore, summing over any one quadrant, whatever the position of the axes,

$$\begin{aligned} NS(F_{m \cdot n}) &= S(f_m \times f_n') \\ &= S(f_m) \times S(f_n') \end{aligned}$$

or

$$N(AB) = (A)(B)$$

and so on, so that Q is zero for all axes. It is impossible to create an artificial association, out of real independence, by mere choice of special axes. This is a most important limitation. At the same time it must be borne in mind that where the variables are not independent, as in the table on p. 277, Q may be changed in sign or rendered vanishingly small by the choice of special (possibly exceptional) axes.*

The whole subject of the connection between correlation and association demands further investigation, as it bristles with difficulties and possibilities of fallacy. In some practical cases there seems no doubt that the signs of Q and r would be different, and, indeed, the physical meaning attached to their interpretation. In the present paper, however, I do not deal further with the subject.

* Cf. also the example of assortative mating according to stature from Mr. GALTON's 'Natural Selection,' p. 82.

Partial Associations and Associations between Groups of Attributes.

§ 29. In the value of Q , as written in equation (1), p. 272, the "Universe of Discourse" is understood, not expressed. If "A" represent, say, deafness, and "B" blindness, we are probably dealing with the association of these infirmities within at most one nation, *e.g.*, English, or even one sex of the nation, *e.g.*, English men. Letters are not given to represent that the universe is so limited, it being generally obvious from the context, but if we take $D = \text{English}$, $E = \text{men}$, we can write Q

$$Q = \frac{(ABDE)(\alpha\beta DE) - (\alpha BDE)(A\beta DE)}{(ABDE)(\alpha\beta DE) + (\alpha BDE)(A\beta DE)} \dots \dots \dots (11),$$

adding the letters DE to every group. Such a coefficient of association will be termed a *partial* coefficient, as distinguished from the *total* coefficient of equation (1). We may speak of partial coefficients of the 1st, 2nd, n th orders, according as the universe is limited by the specification of 1, 2, 3 n attributes. These partial and total coefficients of association correspond roughly in their nature to partial and total coefficients of correlation. In the latter case, however, we limit the universe by specifying that in all members of the universe variable x shall have the fixed magnitude h ; in the former case we only specify that x shall exceed h or be less than h .

The following notation for coefficients of association seems concise and convenient. The total association between A and B we shall denote by AB between two vertical lines—thus $|AB|$. The partial association in the universe of C's, CD's, Cδ's, or Cδε's we shall denote by $|AB|C|$, $|AB|CD|$, $|AB|C\delta|$, $|AB|C\delta\epsilon|$.

§ 30. The number of possible partial coefficients becomes very high as soon as we go beyond four or five variables. Supposing m attributes are given, we can form

$$2^n \frac{(m-2)(m-3) \dots (m-n+1)}{|n|}$$

partial coefficients of the n th order ($n < m-2$) between any one pair of attributes. For we can form 2^n different universes with n attributes, and choose n attributes out of $(m-2)$, in

$$\frac{(m-2)(m-3) \dots (m-n+1)}{|n|}$$

different ways. But the number of possible pairs of attributes (AB , AC , BC , &c.) is $\frac{1}{2}m(m-1)$, and therefore the *total* number of possible partial coefficients of the n th order,

$$2^{n-1} \frac{m(m-1)(m-2) \dots (m-n+1)}{|n|}.$$

These expressions give the following figures:—

Number of attributes m .	Number of partial coefficients of order n : (1) between any one pair of attributes; (2) altogether.									
	$n = 1.$		2.		3.		4.		5.	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
3	2	6								
4	4	24	4	24						
5	6	60	12	120	8	80				
6	8	120	24	360	32	480	16	240		
7	10	210	40	840	80	1680	80	1680	32	672
8	12	336	60	1680	160	4480	240	6720	192	5376

§ 31. But besides these partial coefficients there are others that we may form, where we deal with the association between two *groups* of qualities or attributes, or between a single attribute and a group. These coefficients arise naturally out of the total coefficients; for in any total coefficient a single letter may really represent an aggregate of qualities that we may more completely denote by a group of letters. Thus A may represent deaf-mutism, C imbecility, and $|AC|$ the association between deaf-mutism and imbecility; but if we amplify the notation and use $A =$ deafness, $B =$ dumbness, $C =$ imbecility, the association between deaf-mutism and imbecility will be represented by

$$|AB \cdot C| = \frac{(ABC)(a\beta\gamma) - (a\beta C)(AB\gamma)}{(ABC)(a\beta\gamma) + (a\beta C)(AB\gamma)} \quad \dots \quad (12).$$

This $|AB \cdot C|$ is quite distinct from $|AB|C|$. The latter measures the association between A and B in a group of individuals all possessing C. The former measures the association between C and the compound attribute AB.

A more general form of association coefficient is such a "group coefficient" with the universe specified, *i.e.*, a partial group coefficient. For example

$$|AB \cdot CD|E| = \frac{(ABCDE)(a\beta\gamma\delta E) - (a\beta CDE)(AB\gamma\delta E)}{(ABCDE)(a\beta\gamma\delta E) + (a\beta CDE)(AB\gamma\delta E)} \quad \dots \quad (13).$$

The Method of Serial Chances.

§ 32. There is a very common method of handling such associations as we have here to deal with, more especially where it is desired to discuss the association of some one attribute A with a series of others B, C, D, &c. The chances $(AB)/(B)$, $(AC)/(C)$, &c., are simply tabulated in order of magnitude, and the attribute X for which the chance of X being A, or $(AX)/(X)$, is greatest is held to be the "most important cause of A."

The method seems to have been first brought forward, as a definite statistical method, by QUETELET, in a pamphlet published in 1832, 'Sur la possibilité de mesurer

l'influence des causes qui modifient les élémens sociaux,* but it is either explicitly or implicitly used in most statistical discussions of causation. To take an example from QUETELET's pamphlet, I give below a table of the chances of condemnation of various categories of prisoners in the French Assize Courts during the years 1825-30. Here A must stand for condemnation, B, C, D for the various attributes of the accused (superior education, being a woman, being a man, &c.). The chances tabulated are then $(AB)/(B)$, $(AC)/(C)$, &c., except No. 8, which is $(A)/(U)$. QUETELET went further than a tabulation of the simple chances, and used as a measure of the "degree of influence" of the cause the function

$$\phi = \frac{(AB)/(B) - (A)/(U)}{(A)/(U)} \dots \dots \dots (14),$$

these measures being given in the second column.

Etat de l'accusé.	Probabilité d'être condamné.	Degré relatif d'influence de l'état de l'accusé sur la répression.
1. Ayant une instruction supérieure	·400	- ·348
2. Condamné qui est venu purger sa contumace	·476	- ·224
3. Accusé de crimes contre les personnes	·477	- ·223
4. Sachant bien lire et écrire	·543	- ·115
5. Étant femme	·576	- ·062
6. Ayant plus de 30 ans	·586	- ·045
7. Sachant lire et écrire imparfaitement	·600	- ·023
8. Sans désignation aucune	·614	·000
9. Étant homme	·622	+ ·013
10. Ne sachant ni lire ni écrire	·627	+ ·022
11. Ayant moins de 30 ans	·630	+ ·026
12. Accusé de crimes contre les propriétés	·655	+ ·067
13. Étant contumax	·960	+ ·563

§ 33. Now from the work in § 22, p. 272, we have at once

$$\frac{(AB)}{(B)} - \frac{(A)}{(U)} = \frac{(AB) - (A)(B)/(U)}{(B)} = \frac{(AB) - (AB)_0}{(B)} = \frac{(AB)(a\beta) - (aB)(A\beta)}{(U)(B)} \dots (15),$$

so that if $(AB)/(B) > (A)/(U)$, A and B are certainly positively associated, and if $(AB)/(B) < (A)/(U)$ negatively associated. It does not follow, however, that if $(AB)/(B) > (AC)/(C)$, A and B are more closely associated than A and C. If we write

$$p_1 = (AB)/(B)$$

$$p_2 = (AC)/(C)$$

and if $\kappa_1 \kappa_2$ are the values of the functions κ for AB and AC, then

* It is entitled "Lettre à M. Willermé de l'Institut de France." Bruxelles, 1832. (Royal Statistical Society's Library.—Tracts, S. 4, vol. 5.)

$$\frac{1 + \kappa_1}{1 + \kappa_2} = \frac{p_2(1 - p_1)}{p_1(1 - p_2)} \frac{(1 - p_2)(1 + s_3) + (1 + s_1)}{(1 - p_1)(1 + s_2) + (1 + s_1)}. \quad (16),$$

s_1, s_2, s_3 being the surplus ratios for A, B, and C. Hence if $s_2 = s_3$ the right-hand side is certainly less than unity, and

$$\begin{aligned} \kappa_1 &< \kappa_2 \\ \text{or} \quad Q_1 &> Q_2 \end{aligned}$$

That is to say, *if the surplus ratios of B and C are the same*, $Q_1 > Q_2$ when $p_1 > p_2$; but if they are not, this result does not follow. We can, then, only refer to equation (16). QUETELET's function is for this purpose the same, in effect; as he only divides the difference of the chances by $(A)/(U)$. We may write his function in the form

$$\phi = \frac{(AB)(\alpha\beta) - (A\beta)(\alpha B)}{(A)(B)} \quad (17).$$

§ 34. Now it seems to me that association coefficients and QUETELET's functions, or chances like $(AB)/(B)$, &c., roughly correspond in their uses to correlation coefficients and regressions. The correlation coefficient is a symmetrical function of the variables, ranging between ± 1 , and is zero when the variables are independent. The association coefficient is a symmetrical function of the attributes, ranging between ± 1 , and is zero when the attributes are unassociated. The regressions are zero when the correlation coefficient is zero, but are not symmetrical functions of the variables; they depend on the values of the standard deviations as well as the correlation; and even if the regression of x on y be greater than the regression of x on z , it does not follow that $r_{xy} > r_{xz}$ unless $\sigma_y = \sigma_z$. The QUETELET functions (or simply differences of the chances $(AB)/(B) - (A)/(U)$) are zero when the association coefficient is zero, but are not symmetrical functions of the variables; they depend on the values of the surplus ratios as well as the association; and even if ϕ for AB be greater than ϕ for AC or

$$(AB)/(B) > (AC)/(C),$$

it does not follow that $|AB| > |AC|$ unless $s_C = s_B$. Finally the regressions of x on y, z , &c., may be said to measure the "relative degrees of influence" of unit alterations in y, z , &c., on x , just as QUETELET takes his function to measure the "relative degrees of influence" of B, C, &c., on A. Thus, referring to the table given (p. 281), he remarks, "on voit par là qu'une instruction supérieure exerce une influence cinq fois plus grande que l'avantage d'être femme," since '348 is some five or more times '062.

I confess I do not altogether like QUETELET's function, as there does not seem to me any point in this sort of case in dividing by $(A)/(U)$, or p_0 in our previous notation. If p_0 was in one case '9 and in another '45, it seems absurd to count an attribute that raises p_0 by '05 in either case, half as effective in the former case as the latter; one would rather consider it more effective in the former case.

§ 35. I do not profess to have given in the foregoing pages more than an outline of the theory of the case with which the statistician has to deal; in stronger hands it could probably be carried much further. The method I have suggested has the advantage of bringing the case of association somewhat into line with that of correlation; assimilating the method and conceptions of the case of association to those of the better known field.

The statistician has to handle problems of peculiar difficulty, where the association may have any value. The logician demands $Q = \pm 1$ before he will consent to infer, and limits himself to this special and elementary case. At the opposite pole to that of the logician we may imagine a "logic of independence," where Q is always zero—a case hardly less artificial and quite as interesting as the converse, but one where inference is frequently impossible.

IV.—PROBABLE ERRORS.

§ 36. Let f be the frequency of any one group of any order, and let N be the total frequency observed. Also let $\phi = f/N$. Then the standard deviation of ϕ or σ_ϕ is at once given by

$$\sigma_\phi = \sqrt{\frac{\phi(1-\phi)}{N}} \quad \dots \dots \dots (1).$$

The S.D. of the frequency f is N times this.

§ 37. Now consider the frequencies of two groups and let us find the correlation between errors in their frequencies. We must here consider two different cases, (1) where we are dealing with two ultimate groups, *e.g.*, (AB) (A β), or (ABC) (α BC), or (ABC) ($\alpha\beta\gamma$); (2) where we are dealing with the two non-ultimate groups, *e.g.*, (A) (B), or (AB) (AC), or (AB) (CD).

CASE 1. *Ultimate Groups*.—Let f_1, f_2 be the two frequencies, ϕ_1, ϕ_2 their ratios to N . Suppose ϕ_1 to undergo an increment $\Delta\phi_1$; there is then a total decrement $-\Delta\phi_1$ to be spread over the remaining groups in proportion to their frequencies, the sum of the ϕ 's being constant and equal to unity. Therefore

$$\Delta\phi_2 = -\Delta\phi_1 \cdot \frac{\phi_2}{1-\phi_1} \quad \dots \dots \dots (2).$$

Let $R_{\phi_1\phi_2}$ be the correlation coefficient between errors in ϕ_1 and ϕ_2 . Then the above equation gives us

$$R_{\phi_1\phi_2} \cdot \frac{\sigma_2}{\sigma_1} = -\frac{\phi_2}{1-\phi_1},$$

or for *ultimate groups*

$$R_{\phi_1\phi_2} = -\sqrt{\frac{\phi_1}{1-\phi_1} \cdot \frac{\phi_2}{1-\phi_2}} \quad \dots \dots \dots (3).$$

Hence

$$R_{\phi_1\phi_2} \sigma_1 \sigma_2 = -\frac{\phi_1 \phi_2}{N} \quad \dots \dots \dots (4).$$

an expression that we shall frequently require.

$$\begin{aligned}
\frac{\sigma_{\kappa}^2}{\kappa^2} &= \frac{\sigma_{\phi_1}^2}{\phi_1^2} + \frac{\sigma_{\phi_2}^2}{\phi_2^2} + \frac{\sigma_{\phi_3}^2}{\phi_3^2} + \frac{\sigma_{\phi_4}^2}{\phi_4^2} \\
&\quad + \frac{2}{\phi_2\phi_4} \sigma_{\phi_2}\sigma_{\phi_4} R_{\phi_2\phi_4} + \frac{2}{\phi_1\phi_3} \sigma_{\phi_1}\sigma_{\phi_3} R_{\phi_1\phi_3} \\
&\quad - \frac{2}{\phi_1\phi_2} \sigma_{\phi_1}\sigma_{\phi_2} R_{\phi_1\phi_2} - \frac{2}{\phi_1\phi_4} \sigma_{\phi_1}\sigma_{\phi_4} R_{\phi_1\phi_4} \\
&\quad - \frac{2}{\phi_2\phi_3} \sigma_{\phi_2}\sigma_{\phi_3} R_{\phi_2\phi_3} - \frac{2}{\phi_3\phi_4} \sigma_{\phi_3}\sigma_{\phi_4} R_{\phi_3\phi_4} \\
\frac{\sigma_{\kappa}^2}{\kappa^2} &= \frac{1}{N} \left\{ \frac{1-\phi_1}{\phi_1} + \frac{1-\phi_2}{\phi_2} + \frac{1-\phi_3}{\phi_3} + \frac{1-\phi_4}{\phi_4} + 4 \right\} \\
&= \frac{1}{N} \left\{ \frac{1}{\phi_1} + \frac{1}{\phi_2} + \frac{1}{\phi_3} + \frac{1}{\phi_4} \right\} \\
\sigma_{\kappa} &= \frac{\kappa}{\sqrt{N}} \sqrt{\frac{1}{\phi_1} + \frac{1}{\phi_2} + \frac{1}{\phi_3} + \frac{1}{\phi_4}} \dots \dots \dots (9).
\end{aligned}$$

We may write the above

$$\begin{aligned}
\frac{\sigma_{\kappa}^2}{\kappa^2} &= \frac{(\phi_2\phi_3\phi_4 + \phi_1\phi_3\phi_4 + \phi_1\phi_2\phi_4 + \phi_1\phi_2\phi_3)}{\phi_1\phi_2\phi_3\phi_4} \cdot \frac{1}{N} \\
\sigma_{\kappa}^2 &= \frac{(\phi_2\phi_3\phi_4 + \phi_1\phi_3\phi_4 + \phi_1\phi_2\phi_4 + \phi_1\phi_2\phi_3)}{N} \cdot \frac{\phi_2\phi_4}{\phi_1^3\phi_3^3}.
\end{aligned}$$

Hence, if ϕ_1 or ϕ_3 is zero, $Q = -1$, $\kappa = \infty$, and $\sigma_{\kappa} = \infty$; if ϕ_2 or ϕ_4 is zero, $Q = -1$, $\kappa = 0$, and $\sigma_{\kappa} = 0$.

§ 40. To take Q next, the standard error of which can be derived at once from that of κ ,

$$\begin{aligned}
Q &= \frac{1-\kappa}{1+\kappa} = \frac{2}{1+\kappa} - 1 \\
\delta Q &= -\frac{2}{(1+\kappa)^2} \cdot \delta \kappa \\
\sigma_Q^2 &= \frac{4}{(1-\kappa)^4} \sigma_{\kappa}^2 \dots \dots \dots (10).
\end{aligned}$$

Transform by substituting Q for κ

$$\sigma_Q = \frac{(1-Q^2)}{2\sqrt{N}} \sqrt{\frac{1}{\phi_1} + \frac{1}{\phi_2} + \frac{1}{\phi_3} + \frac{1}{\phi_4}} \dots \dots \dots (11).$$

This again becomes apparently infinite if one of the ϕ 's vanishes, but

$$\frac{(1-Q^2)^2}{\phi_1\phi_2\phi_3\phi_4} = \frac{16 \cdot \phi_1\phi_2\phi_3\phi_4}{(\phi_1\phi_3 + \phi_2\phi_4)^4} = 0$$

whichever of the ϕ 's is zero. So that the probable error of the association coefficient, like that of the coefficient of correlation, vanishes at the limiting values ± 1 .

In the case of equality of contraries we may express the standard error of Q as a function of Q only (*vide* equation 9, p. 275), viz.,

$$\sigma_Q = \frac{1 - Q^2}{\sqrt{N}} \cdot \frac{1 + \sqrt{\kappa}}{2\sqrt{\kappa}} \dots \dots \dots (12).$$

The standard error of the correlation coefficient is simply $(1 - r^2)/\sqrt{N}$, so the S.D. of Q is the greater (for equal numerical values of Q and r) by the fraction on the right. The value of this fraction is given below :—

Ratio of Standard Error of Q to Standard Error of r
(for equal numerical values of Q and r).

Q.	Ratio.	Q.	Ratio.
1	1.001	.6	1.061
.2	1.005	.7	1.095
.3	1.012	.8	1.155
.4	1.023	.9	1.283
.5	1.038	1.0	1.000

For *corresponding* values of Q and r , however, the probable error of Q is less, not greater, than that of r , i.e., if we form Q and r for the same material the probable error of the former constant is the smallest. The table on p. 276, § 26, gives corresponding values of the two coefficients, and these are repeated below with their probable errors :—*

Q.	$\sqrt{N} \times$ probable error.	Value of r corresponding to Q .	$\sqrt{N} \times$ probable error.
.1	.668	.079	.670
.2	.651	.158	.657
.3	.621	.239	.636
.4	.580	.322	.605
.5	.525	.409	.562
.6	.458	.500	.506
.7	.377	.598	.441
.8	.280	.707	.337
.9	.164	.833	.206

In determining the value of the probable error of Q we have, however, implicitly assumed that the dividing points between A and a , &c., were fixed and not liable to

* In both these tables the value used for the probable error of r corresponds to the determination of r by the product-sum method. By any other method, e.g., Mr. W. F. SHEPPARD'S, the probable error is greater, and this would increase the divergence between Q and r , as regards reliability, in the last table.

error. If the dividing points be taken to be the means, this is not so, and the probable error of Q would be increased.

§ 41. The standard error of the surplus ratio comes very simply

$$\begin{aligned}s_1 &= \frac{(A) - (a)}{N} = \frac{2(A)}{N} - 1 = 2\phi - 1 \\ \delta s_1 &= 2 \cdot \delta \phi \\ \sigma_{s_1} &= \frac{2}{\sqrt{N}} \sqrt{\phi(1-\phi)} = \frac{1}{\sqrt{N}} \sqrt{1-s_1^2} \quad \dots \quad (13),\end{aligned}$$

so that the probable error of s_1 is the smaller the larger s_1 .

§ 42. It remains to determine the correlations between errors in surplus ratios and between errors in surplus ratio and errors in association. The first problem proceeds exactly as in the case of finding the correlation between errors in two non-ultimate groups (p. 284, equations (5)-(8)).

$$(A) + (B) - N = (AB) - (\alpha\beta)$$

or say

$$\begin{aligned}\phi_1 + \phi_2 - 1 &= \pi_1 - \pi_3 \\ \therefore \delta s_1 + \delta s_2 &= 2(\delta \pi_1 - \delta \pi_3)\end{aligned}$$

where s_1 s_2 are the surplus ratios of A and B. Proceeding as in the previous case

$$\sigma_{s_1} \sigma_{s_2} R_{s_1 s_2} = \frac{1}{N} (\pi_1 - \phi_1 \phi_2) \quad \dots \quad (14).$$

$$R_{s_1 s_2} = R_{\phi_1 \phi_2} = \frac{\pi_1 - \phi_1 \phi_2}{\sqrt{\phi_1 \phi_2 (1 - \phi_1)(1 - \phi_2)}} \quad \dots \quad (15).$$

Whence

$$\left. \begin{aligned}R_{s_1 s_2} \frac{\sigma_{s_1}}{\sigma_{s_2}} &= \frac{\pi_1 - \phi_1 \phi_2}{\phi_2 (1 - \phi_2)} \\ R_{s_1 s_2} \frac{\sigma_{s_2}}{\sigma_{s_1}} &= \frac{\pi_1 - \phi_1 \phi_2}{\phi_1 (1 - \phi_1)}\end{aligned} \right\} \quad \dots \quad (16).$$

These regressions are positive if A and B be positively associated. Thus if A be, for example, genius in father, B genius in son, and, if in a sample of the population there be found to be a surplus of genius differing from the average by δs_1 , then we should expect to find in the sons of the sample a surplus $s_2 + \delta s_2$, where

$$\delta s_2 = R_{s_1 s_2} \frac{\sigma_{s_2}}{\sigma_{s_1}} \cdot \delta s_1.$$

§ 43. To proceed to find the correlation of errors in Q_{12} and, say, s_1 .

$$\begin{aligned}\delta Q_{12} &= - \frac{2\kappa}{(1+\kappa)^2} \frac{\delta \kappa}{\kappa} \\ &= - \frac{2\kappa}{(1+\kappa)^2} \left\{ \frac{\delta \phi_2}{\phi_2} + \frac{\delta \phi_3}{\phi_3} - \frac{\delta \phi_1}{\phi_1} - \frac{\delta \phi_4}{\phi_4} \right\}.\end{aligned}$$

If

$$f_1 = \frac{(A)}{N} = \frac{(AB)}{N} + \frac{(AB)}{N} = \phi_1 + \phi_2$$

$$\delta s_1 = 2 \delta f_1 = 2 (\delta \phi_1 + \delta \phi_2)$$

$$\delta Q_{12} \cdot \delta s_1 = \frac{4\kappa}{1 + \kappa^2} \cdot \left\{ \frac{(\delta \phi_2)^2}{\phi_2} - \frac{(\delta \phi_1)^2}{\phi_1} + \frac{\delta \phi_1 \cdot \delta \phi_2}{\phi_2} + \frac{\delta \phi_1 \cdot \delta \phi_4}{\phi_4} + \frac{\delta \phi_2 \cdot \delta \phi_4}{\phi_4} - \frac{\delta \phi_1 \cdot \delta \phi_3}{\phi_3} \right. \\ \left. - \frac{\delta \phi_1 \cdot \delta \phi_2}{\phi_1} - \frac{\delta \phi_2 \cdot \delta \phi_3}{\phi_3} \right\}.$$

$$\sigma_{Q_{12}} \cdot \sigma_{s_1} \cdot R_{Q_{12} \cdot s_1} = \frac{4\kappa}{(1 + \kappa^2)^2} \frac{1}{N} \{ (1 - \phi_2) - (1 - \phi_1) - \phi_1 - \phi_1 - \phi_2 + \phi_1 + \phi_2 + \phi_2 \} \\ = 0.$$

Therefore

$$R_{Q_{12} \cdot s_1} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17),$$

that is to say, there is no correlation between errors in association and errors in surplus. Although we were to select out of the whole population a particular group with an abnormally large surplus ratio for any one attribute, we would not expect any definite divergence from the normal in the associations of that attribute observed within the group.

Of course all the expressions we have given above are for *standard errors*; the values of the probable errors will be obtained by multiplying them by the constant .674489. . . .

V.—ILLUSTRATIONS.

A. *Miscellaneous.*

- (1.) Small-pox attack rate and vaccination.
- (2.) Examples from Mr. GALTON'S "Natural Inheritance" :—
 - Assortative mating according to temper.
 - Association of temper in fraternities.
 - Inheritance of artistic faculty.
 - Assortative mating according to stature.
- (3.) Examples from DARWIN'S "Cross and Self Fertilisation" :—
 - Cross fertilisation of parentage and tallness of offspring.
 - Pure self fertilisation and crossing of flowers on same plant.

(A). *Miscellaneous.*

§ 44.—(1.) Small-pox and vaccination.

At the very commencement of this paper death-rates, with and without the administration of an antitoxin, were suggested as affording suitable examples of "association." Death-rates by small-pox amongst the vaccinated and unvaccinated would form such

an instance, but the figures I found most suitable to my purpose are attack-rates—not death-rates. The following table gives the (percentage) small-pox attack rate, in *houses actually invaded by small-pox*, of persons under and over 10 years of age, in five towns in which small-pox epidemics have recently occurred.*

Town.	Date.	Attack rate under 10.		Attack rate over 10.	
		Vaccinated.	Unvaccinated.	Vaccinated.	Unvaccinated.
Sheffield	1887-88	7.9	67.6	28.3	53.6
Warrington	1892-93	4.4	54.5	29.9	57.6
Dewsbury	1891-92	10.2	50.8	27.7	53.4
Leicester	1892-93	2.5	35.3	22.2	47.0
Gloucester	1895-96	8.8	46.3	32.2	50.0

From these data we can work out the association between “lack of vaccination” and “attack,” for children and persons over 10 years of age. If we call attack A, “non-vaccination” B, the data given are $100 (A\beta)/(\beta)$ and $100 (AB)/(B)$; subtracting each percentage from 100, we get $100 (a\beta)/(\beta)$ and $100 (aB)/(B)$. Thus for the coefficient of association in Sheffield for children we have

$$Q = \frac{67.6 \times 92.1 - 32.4 \times 7.9}{67.6 \times 92.1 + 32.4 \times 7.9} \\ = .92$$

where we have divided through numerator and denominator of the ordinary expression for Q by $(B)(\beta)$, leaving its value unaltered. This seems rather an interesting case, as the form in which the data are presented does not give the surplus ratio for non-vaccination, *i.e.*, the ratio of non-vaccination to vaccinated, but does give the association coefficient Q. The whole series of values are given below, and form a striking addition to the previous table. The association between non-vaccination and attack is very high indeed for young children—.8 to .9—but drops sharply to

Association between Non-vaccination and Attack in Infected Households.

Town.	Children under 10.	Persons over 10.
Sheffield92	.49
Warrington93	.52
Dewsbury80	.50
Leicester91	.51
Gloucester80	.36

* I have taken the table from Mr. NOEL A. HUMPHREY's paper, “Vaccination and Small-Pox Statistics,” ‘Journal Royal Statistical Soc.’ vol. 60 (1897), p. 525. It is quoted by him from the ‘Final Report of the Vaccination Commission,’ p. 65.

·5 (owing presumably to the waning protection of the vaccination made in infancy) in the older age group.

The constancy of the association in towns with widely different attack rates is a point worthy of notice. Sheffield, Warrington, and Leicester exhibit practically identical associations, although the attack rates vary from 7·9 to 2·5 and 67·6 to 35·3. Not having the original figures for these cases I cannot state the probable errors.

§ 45.—(2.) From Mr. GALTON's "Natural Inheritance."

Assortative Mating according to Temper.—On p. 231 of "Natural Inheritance" Mr. GALTON gives the data, based on 111 marriages :—

Good-tempered husbands with bad-tempered wives	. .	24 per cent.
Bad-tempered	„ good-tempered	„ . . 31 „
Good-tempered	„ „	„ . . 22 „
Bad-tempered	„ bad-tempered	„ . . 23 „

Here

$$Q = \frac{22 \times 23 - 24 \times 31}{22 \times 23 + 24 \times 31} = - \cdot 19$$

for the association between temper in husband and wife, *i.e.*, on the whole bad-tempered husbands have good-tempered wives, and *vice versa*. But the probable error of the association =

$$\cdot 6745 \frac{1 - \cdot 0361}{2} \sqrt{\frac{100}{111}} \sqrt{\frac{1}{22} + \frac{1}{23} + \frac{1}{24} + \frac{1}{31}} = \cdot 124$$

so that only very slight stress can be laid on the sign of the association.

The advantage of having the whole question of the association thus compressed into one figure, with a definite probable error, is here very clearly marked. Comparing the actual figures with the distribution in the case of no association, Mr. GALTON concluded "that the figures taken from observation run as closely with those derived through calculation as could be expected from the small number of observations." *

§ 46. *Association of Temper in Fraternities.*—On p. 235 of "Natural Inheritance" Mr. GALTON gives, in the same investigation, data for the association of temper in a fraternity (group of brothers and sisters). Thus in sixty-six fraternities of three members there were eleven cases reported in which all were good-tempered; fifteen in which one was good and two bad; twenty-one in which one was bad and two good; and eight in which all were bad. From data of this kind I formed all the possible pairs (permutations). Thus in the above case, using G for good, γ for bad, I find the number of pairs as below :—

* This conclusion is in part affected by a slight error (owing to accumulation) in the "non-associated" figures given. The (constant) difference between the observed and "non-associated" frequencies is 2 per cent. to the nearest unit.

Number of fraternities of three.	Giving pairs GG.	Giving pairs Gγ.	Giving pairs γG.	Giving pairs γγ
All good 11	66
2 good, 1 bad 15	30	30	30	...
1 good, 2 bad 21	...	42	42	42
All bad 8	48
Total	96	72	72	90

Getting out the number of pairs in the same way for fraternities of all the sizes given, I find the totals:—

Good-good 330 pairs.
 Good-bad and bad-good . . . 255 „ each.
 Bad-bad 454 „

$$\therefore Q = \frac{330 \times 454 - 255 \times 255}{330 \times 454 + 255 \times 255}$$

$$= \cdot 395.$$

This value seems rather low; the fraternal correlation of $\cdot 4$ should correspond to an association of about $\cdot 49$, or more as the axes of division are not taken through the medians.

§ 47. *Inheritance of Artistic Faculty* (“Natural Inheritance,” p. 218).—The data are:—

Number of artistic children with artistic parentage	296
„ „ „ non-artistic parentage.	173
„ non-artistic children with artistic „	372
„ „ „ non-artistic parentage	666

We have called the parentage artistic where *either* parent is so entered. Mr. GALTON's table does not separate the sexes. The above is consequently a kind of “mid-parentage” inheritance table. The association coefficient is

$$Q = \cdot 508 \pm \cdot 029.$$

The correlation of offspring with mid-parent is $\cdot 42$, corresponding to an association of $\cdot 51$ —or remarkably close to the above; but the close agreement must be more or less accidental. As we have seen (p. 276, and example), shifting the axes of division of a correlation surface towards the extremities of the surface, so as to increase or decrease the surplus ratio of each attribute, increases the association between them. This ought to have made the association somewhat higher in the present case, as there are only 469 artistic children to 1038 non-artistic, or $s = \cdot 378$. It is interesting

to note that apparently, from Mr. GALTON's figures, there is a negative correlation between the artistic character of parentage and fertility ; thus :—

When both parents are artistic, number of children to fraternity is	4.93
„ one parent is „ „ „ „ „	5.15
„ neither „ „ „ „ „	5.28

This would not, however, affect the association between artistic faculty of parentage and offspring, as increasing or decreasing the frequencies 296 and 372 in any constant ratio would not alter the ratio of the cross-products. The interest lies in the fact that artistic faculty is apparently a heritable attribute associated (negatively) with fertility, and hence (as Professor PEARSON has pointed out) would tend to disappear in the absence of opposing causes.

§ 48. *Assortative Mating according to Stature.*—I give this example as an instance of the fact that the association between attributes depends *very largely*, in some cases, on what I have called the choice of axes, *i.e.*, the strictness of definition of the attribute. The following are the data giving the number of observed cases in which a tall, medium, or short husband was mated with a tall, medium, or short wife (“Natural Inheritance,” p. 206).

		Wife.		
		Tall.	Medium.	Short.
Husband.	Tall	18	28	14
	Medium	20	51	28
	Short	12	25	9

Now, if we take the dividing point between the “tall” or “fairly tall,” and “fairly short” or “short” to be (1) between tall and medium, (2) between medium and short, we get the following data :—

	(1)	(2)
Tall husband and tall wife	18	117
„ „ „ short wife	42	42
Short „ „ tall „	32	37
„ „ „ short „	113	9
	205	205

In the first case

$$Q = + \cdot 20 \pm \cdot 11$$

In the second

$$Q = - \cdot 19 \pm \cdot 13.$$

Thus the first case gives a positive, the second a negative association between stature of husband and stature of wife, in both cases the value of Q is greater than its probable error, and the difference between the two Q 's is more than twice the probable error of the difference.

I think the above change of sign implies that while tallness in husband is associated with tallness in wife, (extreme) shortness is not associated with (extreme) shortness. Thus 30 per cent. of the tall husbands have tall wives, but only 20 per cent. of the short husbands have short wives; 36 per cent. of the tall wives have tall husbands, but only 18 per cent. of the short wives have short husbands. While it appears at first sight an unsatisfactory characteristic of association that its sign may depend on the axes chosen, I believe that this is not really the case. On the contrary, such changes of sign may call attention to important physical realities, masked by the application (possibly) of the "rectilinear" theory of correlation, to cases where it gives a result of a somewhat crudely average character. Where only one average sort of result is similarly desired for the association I think the lines of division between A and α , and so on, should be taken through the means or medians.

§ 49.—(3.) DARWIN'S "Cross and Self Fertilisation of Plants."

The attributes, the association of which is here discussed, are "crossing of parentage" and "tallness of height" in plants. Thus, the one attribute is *really* invariable; the parentage must be *either* crossed *or* self-fertilised—since asexual propagation is excluded. The other attribute—height—is, however, really variable, and hence, in accordance with the preceding remarks, the point of division between tallness and shortness is best taken at the mean.

In many of the species the number experimented on by DARWIN is too small to give any reliable coefficient of association. I have therefore picked out only a few of the species for which most data were available and investigated them, to see whether there were any reliable differences between the associations observed for different species, and as a rough ground for comparison I have pooled together the results for the thirty-eight different species for which there were sufficient data, and worked out the association for the total. The data are given in the table below.

The "average height" referred to is the average height of cross and self-fertilised plants taken all together; if their numbers were unequal the cross and self-fertilised were averaged separately, and the mean of the two averages taken. Different generations are also all pooled together for each species, but each of the tables in the book (different generations or experiments) was averaged separately, and the heights in it referred to its own averages.*

* For other details I must refer to the book itself. Thus, in some tables a pot of "crowded plants," in

The associations I find for the whole mass and for the five species chosen are

	Number of plants.	
Whole series.	1094	$Q = + \cdot 66 \pm \cdot 025$
<i>Ipomea purpurea</i>	146	$= + \cdot 90 \pm \cdot 028$
<i>Petunia violacea</i>	154	$= + \cdot 90 \pm \cdot 026$
<i>Reseda lutea</i>	64	$= + \cdot 74 \pm \cdot 086$
<i>Reseda odorata</i>	110	$= + \cdot 49 \pm \cdot 103$
<i>Lobelia fulgens</i>	68	$= + \cdot 29 \pm \cdot 153$

Are these differences significant? Taking successive differences down the table from *Petunia violacea* onwards I find

	Difference.	Probable error of difference.
<i>Petunia violacea</i> and <i>Reseda lutea</i> . . .	$\cdot 16$	$\cdot 090$
<i>Reseda lutea</i> and <i>Reseda odorata</i> . . .	$\cdot 25$	$\cdot 134$
<i>Reseda odorata</i> and <i>Lobelia fulgens</i> . . .	$\cdot 20$	$\cdot 184$

and for the extreme difference

<i>Petunia violacea</i> and <i>Lobelia fulgens</i> . .	$\cdot 61$	$\cdot 155$
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These figures can leave no doubt, I think, that specific differences do exist as regards closeness of association between crossing and vigour of offspring—even in species all normally cross fertilised. The difference between *Ipomea purpurea* or *Petunia violacea* and *Lobelia fulgens* is certainly significant, and not only so but each successive difference in the above short table is greater than its probable error. It must be remembered that we are dealing with a different point to that noted by DARWIN; he is dealing with the *amount* of the difference between crossed and self fertilised offspring; we are measuring the approach towards absoluteness of the law that there is a constant difference. The law is much less absolute—permits of many more individual exceptions—with some species than with others.

A curious point is the significant difference between the wild and cultivated species of *Reseda*. The difference may possibly be due to the cultivated character of *R. odorata*, but certainly need not be, as the two first species on the list in which the association between height and crossing is $\cdot 9$ are both cultivated species foreign to England. *Reseda odorata* was also erratic in its behaviour as regards self sterility (*cf.* "Cross and Self Fertilisation," p. 119 and pp. 336–9), some plants being highly self fertile, others quite self sterile. The offspring of highly and slightly self fertile plants were, however, equally vigorous.

In the table on p. 295 I have entered the sign of the association in the column on the left; as I have stated, the probable errors are so large that it seems misleading to give which only the tallest of each lot was measured, is included. In other cases I have pooled outdoor-grown plants with plants in pots, taking the average height separately as above, and so on.

Association between Cross Fertilisation and Tallness of Height (CHARLES DARWIN,
"Cross and Self Fertilisation").

Species.	Sign of association.	Total observed.	Cross fertilised.		Self fertilised.	
			Above average of their generation or series.	Below average of their generation or series.	Above average of their generation or series.	Below average of their generation or series.
1. <i>Ipomea purpurea</i> . . .	+	146	63	10	18	55
2. <i>Digitalis purpurea</i> . . .	+	24	12	4	2	5
3. <i>Verbascum thapsus</i> . . .	+	12	4	2	3	3
4. <i>Gesneria pendulina</i> . . .	+	16	5	3	3	5
5. <i>Salvia coccinea</i> . . .	+	12	4	2	2	4
6. <i>Origanum vulgare</i> . . .	0	8	2	2	2	2
7. <i>Brassica oleracea</i> . . .	-	18	4	5	5	4
8. <i>Iberis umbellata</i> . . .	+	14	5	1	3	4
9. <i>Papaver vagum</i> . . .	+	30	9	6	5	9
10. <i>Eschscholzia californica</i> . . .	+	8	3	1	1	3
11. <i>Reseda lutea</i> . . .	+	64	25	7	11	21
12. <i>Reseda odorata</i> . . .	+	110	39	16	25	30
13. <i>Viola tricolor</i> . . .	+	28	12	2	1	13
14. <i>Delphinium consolida</i> . . .	+	12	3	3	2	4
15. <i>Viscaria oculata</i> . . .	0	30	8	7	8	7
16. <i>Dianthus caryophyllus</i> . . .	+	16	5	3	4	4
17. <i>Hibiscus africanus</i> . . .	-	8	2	2	3	1
18. <i>Pelargonium zonale</i> . . .	+	14	4	3	3	4
19. <i>Tropæolum minus</i> . . .	+	16	6	2	2	6
20. <i>Limnanthes douglasii</i> . . .	+	31	12	4	4	11
21. <i>Lupinus luteus</i> . . .	+	16	8	0	2	6
22. <i>Phaseolus multiflorus</i> . . .	0	10	3	2	3	2
23. <i>Lathyrus odoratus</i> . . .	+	16	5	3	2	6
24. <i>Clarkia elegans</i> . . .	+	8	3	1	1	3
25. <i>Bartonia aurea</i> . . .	-	16	3	5	4	4
26. <i>Scabiosa atropurpurea</i> . . .	+	8	2	2	1	3
27. <i>Lactuca sativa</i> . . .	-	13	3	4	3	3
28. <i>Specularia perfoliata</i> . . .	+	8	2	2	1	3
29. <i>Lobelia ramosa</i> . . .	+	14	5	2	1	5
30. <i>Lobelia fulgens</i> (2nd gen.) . . .	+	68	17	17	12	22
31. <i>Nemophila insignis</i> . . .	+	22	11	1	2	8
32. <i>Borago officinalis</i> . . .	+	8	2	2	1	3
33. <i>Nolana prostrata</i> . . .	-	10	2	3	3	2
34. <i>Petunia violacea</i> . . .	+	154	61	16	13	64
35. <i>Nicotiana tabacum</i> . . .	-	34	7	10	8	9
36. <i>Beta vulgaris</i> . . .	+	16	5	2	4	4
37. <i>Zea mays</i> . . .	+	30	12	3	3	12
38. <i>Phalaris canariensis</i> . . .	+	46	15	8	7	16
Totals . . .	+	1094	395	168	179	372

the amounts in all cases. In six cases of the thirty-eight the sign is negative, and in three cases the association is zero.

§ 50. There is another interesting point of the same investigation in which the present method will enable us to state clearly the quantitative result and its probable

error. This is the question whether fertilisation of a flower with pollen from another flower on the same plant is any better than strict self-fertilisation. DARWIN came to the conclusion that in only one of the five species tried—*Digitalis purpurea*—was there any sensible advantage in crossing different flowers. The point was a difficulty, as there should be an advantage, though a slight one, on his theory that the benefit of cross-fertilisation arises from differences in the general constitution of flowers crossed.

In only three of the five species tried are the numerical data given in the form required for the present method. They run as below :—

	Species.			Total.	
	<i>Ipomea purpurea.</i>	<i>Mimulus luteus.</i>	<i>Digitalis purpurea.</i>		
Table in book	XII.	XXI., XXII.	XXIV.		
Cross {	Above average	17	21	19	57
	Below average	14	16	6	36
Self {	Above average	22	16	11	49
	Below average	9	21	14	44
Total	62	74	50	186	
Association coefficient Q . .	- .34 ± .160	+ .27 ± .147	+ .60 ± .133	.174 ± .097	
Difference of Q's and prob- able error of difference	} .61 ± .217 .33 ± .198				

Thus, in the case of *Ipomea purpurea*, the association is distinctly negative—crossing with another flower of the plant was worse than pure self-fertilisation—but in both the other cases it is positive. *Mimulus*, it is true, offers somewhat doubtful evidence (two experiments having given conflicting results), but the coefficient of association is almost twice its probable error. The foxglove certainly exhibits far the highest and most significant association. Two out of the three species give a positive result, and if all the species are pooled together the result is positive. The fact is we are looking, in all probability, for a very small association, and extensive experiments may be necessary to render its existence certain. Taking the above results together, I should certainly say they gave evidence on the whole of a positive association. The odds against the negative association in the case of *Ipomea* occurring as a purely

chance deviation from the positive would be, roughly, twenty-one to four, or say five to one only—not overwhelming odds by any means.

As in the general case of complete crossing *versus* self-fertilisation, the differences between species are, however, almost certainly significant. It may be true that “crossing of different flowers on the same plant is always, *on the average*, better than pure self-fertilisation,” but the closeness with which the law holds good will vary in different species.

VI.—ILLUSTRATIONS—*continued*.

(B.) *The Association of Defects in Children and Adults.*

§ 51. The material on which the following investigation is based is drawn almost wholly from the “Report on the Scientific Study of the Mental and Physical conditions of Childhood,”* issued by a committee with representatives from the British Medical Association, the British Association, the Charity Organization Society, &c. Before 1892 the same work was in the hands of other committees of those bodies, and in 1897, a “Childhood Society” was formed to carry it on. Two series of investigations have been made under these committees, the first from 1888–91, the second from 1892–94. As I understand, the whole of the observations in the first period, and the great majority of them in the second, have been made by Dr. FRANCIS WARNER.

For the complete description of the method of observation, &c., I must refer to the report itself. A very large number of schools were visited (Board Schools, Poor Law Schools, Voluntary Schools, &c., most, but not all, in London), and the children in them examined individually for the presence or absence of certain defects, of which the main classes were (using Dr. WARNER’s notation).†

- A. *Defects in development* of the body or its parts ; in size, form, or proportioning of parts.
- B. *Abnormal nerve signs* ; certain abnormal actions, movements, and balances.
- C. *Low nutrition*, as indicated by the child being thin, pale, or delicate.
- D. *Mental dulness*. The teachers’ report as to mental ability was added to the record of each child registered, and those stated to be below the average in ability for school work were registered as “Dull.”

These main classes of defects observed were the same in both investigations, in each of which 50,000 children were observed. The returns given are, however, somewhat more detailed for the later investigation, the material being sub-divided, for instance, into school standards. I have used material from both.

§ 52. The whole of this mass of observations was made, as stated, on children not

* Published by the Committee, Parkes Museum, Margaret Street. Price 2s. 6d.

† Report ; pp. 12–13. A fuller description of the signs is given on pp. 13–16 and pp. 72 *et seq.*

older than fourteen years or so. For purposes of comparison, and in order to be able to follow the association of defects from childhood to old age, I have made some use of the material available in the Census.* This consists of the numbers of those who are blind, deaf and dumb, or mentally deranged, and the numbers of those suffering from combinations of these defects; the sexes are separated and the numbers in different age groups are given. The figures are very unreliable in the early age groups (0—5, 5—10, 10—15), especially for "mental derangement,"† but so far as I know they are the only figures of the kind published. I have not used the age group 0—5 at all, and the others appear to give much the sort of associations one would expect, quite comparable with those given by the results of Dr. WARNER's investigations.

§ 53. The case to be treated is by no means a simple one. Suppose a certain group of young children to be observed at some time and the frequencies of all combinations of certain defects noted; let the survivors be again observed after a lapse of years, and the defects be again noted. Changes in the relative frequencies and the associations observed between defects will have taken place for three reasons—

- (1) Because some of those originally observed have died;
- (2) Because some have outgrown or lost certain defects;
- (3) Because others have acquired defects.

We have taken the case as referring to children, but the first and third causes of change are equally, or more, effective in the case of adults.

Now if the observations were made as supposed, and a record kept of *the same individuals*, the effect of each change could be distinguished. Those who had either lost or acquired defects‡ during the intervening period could be struck out of both series; the resulting changes would be due to selection only, and so on. But unfortunately this is not the case in any published statistics of which I am aware, even in the "Childhood Committee's" work, where such a procedure might well have been adopted. All that is given is that a certain group, closely centered round a

* Census of 1891, vol. 3, Tables 15, 16, p. lvii.; 1881, vol. 3, Tables 14, 15, p. xlv. In the Census of 1871 the numbers with combinations of defects are not given, so the material is not available for the present purpose. In the Census of 1881 those who are "Idiot or Imbecile" are distinguished from the "Insane," both in the first and second order groups, and I have made some use of this (*cf.* below, p. 312). In 1891 those "Mentally Deranged from Childhood" and "Blind from Childhood" are distinguished from others, but the same distinction is not continued where these defects are combined with others. The notation of the Census is not clear: by the courtesy of the Registrar-General I am informed that "Blind" includes "Blind and Dumb," and so on; but "Blind and Dumb" does *not* include "Blind, Dumb, and Mentally Deranged," *i.e.*, the frequencies given are (A) (B) (C) (AB γ) (A β C) (α BC) (ABC). This should be made clear in a future Census.

† *Cf.* remarks in the Census Reports for 1881: General Report, p. 68.

‡ I speak of "defects" as they form our subject matter, but the reasoning applies to attributes of any kind. I would define a defect, tentatively, as an attribute the possessors of which have a death-rate above normal, but I do not *know* that this applies to all, *e.g.*, of the defects noted by Dr. WARNER.

certain age, has certain percentages of defectives and exhibits certain associations between defects. Another group, of another mean age, has different percentages of defects and different associations. Such differences are due to all three of the above causes of change acting together, superposed in general on wholly unknown initial differences between the groups, due either to their being differently gathered samples, or to a secular change taking place in the population. It becomes, then, impossible to separate, except conjecturally and in a more or less tentative manner, the effects of selection from those of *growth*—including under this term all processes of change that take place in the individual.

§ 54. Let $(AB)_1, (A\beta)_1, (\alpha B)_1, (\alpha\beta)_1$ be the four second-order frequencies observed for any pair of defects for an early age, and let $(AB)_2, (A\beta)_2, (\alpha B)_2, (\alpha\beta)_2$ be the frequencies at a later age in the same individuals, or in an older age group of the same population. Then if Q_1, Q_2 be the association coefficients for the two groups, κ_1, κ_2 the values of the corresponding ratio of the cross products

$$\begin{array}{l} \text{if} \\ Q_2 < Q_1 \\ \kappa_2 > \kappa_1 \end{array}$$

$$\text{or} \quad \frac{(\alpha B)_2 (A\beta)_2}{(AB)_2 (\alpha\beta)_2} > \frac{(\alpha B)_1 (A\beta)_1}{(AB)_1 (\alpha\beta)_1}$$

$$\frac{(\alpha B)_2}{(\alpha B)_1} \cdot \frac{(A\beta)_2}{(A\beta)_1} > \frac{(AB)_2}{(AB)_1} \cdot \frac{(\alpha\beta)_2}{(\alpha\beta)_1}.$$

Let

$$\frac{(AB)_2}{(AB)_1} = s_1, \quad \frac{(A\beta)_2}{(A\beta)_1} = s_2, \quad \frac{(\alpha B)_2}{(\alpha B)_1} = s_3, \quad \frac{(\alpha\beta)_2}{(\alpha\beta)_1} = s_4.$$

Then

$$Q_2 < Q_1$$

so long as

$$s_1 s_3 < s_2 s_4.$$

If we are dealing with a population subjected solely to selection, s_1, s_2, s_3, s_4 are the survival rates for the four classes; the quantities $s_2/s_1, s_3/s_1, s_4/s_1$ we may call the "survival figures" for the three classes, and the condition may be written

$$\sigma_3 < \sigma_2 \sigma_4.$$

That is, if the survival figure for the class with two defects be less than the product of the survival figures for the singly defective classes, the association will decrease. *A priori* I could not say whether this condition should hold or not; it appears possible that selection might either decrease or increase association. Practically the condition does seem to hold,* but, as mentioned above, the evidence is not complete nor certain, for we cannot, amongst present data, find a single case in which change is certainly due to selection alone without other causes.

When we are comparing one age group with another of the same population the

* Below p. 312-315.

s's are no longer, of course, simple survival rates, and may be greater than unity. This is notably the case for instance with such defects as increase rapidly in old age, *e.g.*, blindness or mental derangement.

§ 55. Let us turn now to the consideration of Dr. WARNER's materials. In Table I. below I give the associations observed between the six possible pairs of defects in the two successive investigations, together with the probable errors of the association coefficients. At the bottom of the table are given the percentages of the children, observed with given defects A, B, C, or D, and with any defect or combination of defects.* The associations observed are on the whole very markedly lower in the second investigation, and the percentages of children with given defects are smaller (except for dulness), but owing to the lower association the total percentage of defective children has risen, in the case of the girls, from 14·3 to 14·8 per cent.

TABLE I.—Comparison of the Association Coefficients in the Investigations of 1888-91 and 1892-94. A. Development Defects. B. Nerve Signs. C. Low Nutrition. D. Mental Dulness.

	Boys.		Girls.	
	1888-91.	1892-94.	1888-91.	1892-94.
AB 	·898 ± ·003	·750 ± ·005	·904 ± ·003	·784 ± ·008
AC 	·903 ± ·004	·848 ± ·007	·952 ± ·002	·916 ± ·004
AD 	·893 ± ·003	·846 ± ·005	·929 ± ·003	·900 ± ·004
BC 	·862 ± ·006	·783 ± ·010	·914 ± ·004	·814 ± ·009
BD 	·893 ± ·003	·897 ± ·003	·926 ± ·003	·905 ± ·004
CD 	·791 ± ·009	·823 ± ·008	·863 ± ·006	·835 ± ·008
Percentage of children with defect	A . .	13·5	9·6	6·8
	B . .	12·6	9·0	8·5
	C . .	3·8	4·4	3·2
	D . .	8·2	6·3	6·9
With any defect. . .	19·9	18·2	14·3	14·8

The associations are, however, all high (very high compared with most coefficients of organic correlation with which one has to deal), ranging from ·784 to ·952.

* *I.e.*, the last figure is $100(1 - (\alpha\beta\gamma\delta)/N)$.

§ 56. The differences between the associations cannot probably be, at present at all events, assigned to any definite cause or any definite difference in the material observed. We would expect to find differences of association in different groups, just as we find differences between the correlation coefficient for different local races, without our being able to say with certainty how these differences have come about. In many cases the differences are certainly real, as they are large compared with the probable errors of the differences—three to eight times the probable errors. That considerable differences exist between different classes of schools, not only in the proportions of defective children but in the associations between defects, is shown by Table II. (based on Table 19 of the Report), and consequently the divergence between the results of the two investigations may be due to the different classes of schools observed. Such differences between schools may in their turn be partly or wholly due to differences of age or nationality between the children. The effects of age we deal with below (pp. 309, *et seq.*) ; the differences between nationalities* are illustrated by Table III. (based on Tables 27, 28 of the Report), showing the associations for English, Jews, and Irish :—

§ 57. These two tables suggested to me at first sight an apparent law—that associations were on the whole higher where populations were healthier or less defective. If we take Table II., 4 of the 6 associations in Poor Law schools are greater than those in Industrial schools ; 4 of the associations in Homes and Orphanages are greater than those of the Poor Law schools, equality subsisting in one of the remaining cases ; and 5 of the associations in Elementary schools are greater than those in Homes and Orphanages, taking the schools in order of healthiness. The case is not so marked for girls, and we must note that for them the Homes and Orphanages are *more* defective than Poor Law schools. In Table III. for the boys, Jews are more defective than English, and Irish than Jews ; the Jews are less associated than the English in 4 cases of the 6, and the Irish less associated than the Jews in 4 cases out of 6 also. But again the case breaks down for girls. English girls are more defective than Jewish girls, but their associations are less in just 3 out of the 6 cases ; Irish girls are more defective than English, but their associations are actually greater in the majority of cases.

If we compare in this way only those cases that are adjacent in the order of defectiveness we get

TABLE II.—

			Boys.		Girls.
Associations greater where defectiveness less in			12 cases,		in 9 cases.
„ less or equal „ „ „			6	„	9 „

TABLE III.—

Associations greater where defectiveness less in	8	„	5	„
„ less or equal „ „ „	4	„	7	„

* It must be noted that they were all *London* children

TABLE II.—Illustrating the Variation of the Association between Defects in different Groups of Schools (1888-91 investigation). At the bottom of the Table are given the Percentages of Children with given Defects or with any Defect in each Group. A. Development Defects. B. Nerve Signs. C. Low Nutrition. D. Mental Dulness.

Association coefficients.	Boys.				Girls.			
	Certified industrial schools.	Poor Law schools.	Homes and orphanages.	Public elementary schools.	Certified industrial schools.	Poor Law schools.	Homes and orphanages.	Public elementary schools.
AB	$\cdot 860 \pm \cdot 013$	$\cdot 915 \pm \cdot 005$	$\cdot 958 \pm \cdot 008$	$\cdot 885 \pm \cdot 004$	$\cdot 920 \pm \cdot 018$	$\cdot 926 \pm \cdot 006$	$\cdot 920 \pm \cdot 012$	$\cdot 895 \pm \cdot 004$
AC	$\cdot 762 \pm \cdot 046$	$\cdot 865 \pm \cdot 014$	$\cdot 916 \pm \cdot 032$	$\cdot 921 \pm \cdot 004$	$\cdot 923 \pm \cdot 022$	$\cdot 910 \pm \cdot 012$	$\cdot 946 \pm \cdot 015$	$\cdot 960 \pm \cdot 002$
AD	$\cdot 856 \pm \cdot 015$	$\cdot 893 \pm \cdot 007$	$\cdot 935 \pm \cdot 013$	$\cdot 893 \pm \cdot 004$	$\cdot 882 \pm \cdot 026$	$\cdot 925 \pm \cdot 007$	$\cdot 936 \pm \cdot 010$	$\cdot 930 \pm \cdot 003$
BC	$\cdot 894 \pm \cdot 040$	$\cdot 881 \pm \cdot 011$	$\cdot 540 \pm \cdot 124$	$\cdot 874 \pm \cdot 006$	$\cdot 919 \pm \cdot 023$	$\cdot 863 \pm \cdot 017$	$\cdot 882 \pm \cdot 026$	$\cdot 924 \pm \cdot 004$
BD	$\cdot 864 \pm \cdot 014$	$\cdot 894 \pm \cdot 007$	$\cdot 894 \pm \cdot 019$	$\cdot 895 \pm \cdot 004$	$\cdot 941 \pm \cdot 013$	$\cdot 929 \pm \cdot 007$	$\cdot 918 \pm \cdot 013$	$\cdot 925 \pm \cdot 004$
CD	$\cdot 761 \pm \cdot 045$	$\cdot 659 \pm \cdot 029$	$\cdot 821 \pm \cdot 055$	$\cdot 830 \pm \cdot 008$	$\cdot 758 \pm \cdot 058$	$\cdot 861 \pm \cdot 018$	$\cdot 882 \pm \cdot 026$	$\cdot 871 \pm \cdot 007$
Per cent. A	20.7	15.2	13.8	12.3	15.2	12.0	11.9	8.8
Per cent. B	20.9	14.8	14.5	11.2	14.0	9.8	10.7	8.5
Per cent. C	2.6	4.0	2.2	3.9	7.6	3.5	3.6	2.2
Per cent. D	14.0	8.4	8.9	7.6	11.5	7.1	10.7	5.7
With any defect }	29.9	21.9	18.6	18.5	20.9	16.4	17.7	13.7

TABLE III.—Illustrating the Variation in Associations between Defects in different Nationalities (1892-94).

A. Development Defects. B. Nerve Signs. C. Low Nutrition. D. Dulness.

Association.	English.	Jews.	Irish. .
AB { Boys. . .	·752 ± ·008	·734 ± ·023	·729 ± ·023
Girls. . .	·768 ± ·009	·835 ± ·018	·860 ± ·017
AC { Boys. . .	·862 ± ·008	·832 ± ·025	·750 ± ·037
Girls. . .	·916 ± ·005	·914 ± ·015	·903 ± ·016
AD { Boys. . .	·849 ± ·006	·863 ± ·014	·785 ± ·022
Girls. . .	·894 ± ·005	·910 ± ·001	·929 ± ·010
BC { Boys. . .	·787 ± ·011	·796 ± ·029	·735 ± ·047
Girls. . .	·808 ± ·010	·822 ± ·029	·863 ± ·021
BD { Boys. . .	·904 ± ·004	·847 ± ·015	·894 ± ·017
Girls. . .	·906 ± ·004	·881 ± ·013	·914 ± ·011
CD { Boys. . .	·843 ± ·009	·710 ± ·042	·770 ± ·035
Girls. . .	·840 ± ·009	·771 ± ·038	·839 ± ·026
Per cent. { Boys. . .	8·4	9·2	11·6
A Girls. . .	6·8	6·3	8·4
Per cent. { Boys. . .	10·2	11·9	14·8
B Girls. . .	8·4	7·9	9·0
Per cent. { Boys. . .	2·8	3·0	3·3
C Girls. . .	3·4	2·4	3·9
Per cent. { Boys. . .	8·0	8·1	8·4
D Girls. . .	7·0	6·6	6·5
Number { Boys. . .	20,682	2,631	2,171
observed { Girls. . .	18,286	2,668	1,952

Thus the statistics of the girls do not at all support the first impression given by the figures for boys, and the whole of Table I. is directly adverse to any such hypothesis. In 10 cases out of the 12 of that table the associations are smaller in the second investigation, but in 6 cases out of 8 the proportions of defects are also smaller. Finally, it must be remembered that the theorem given on p. 288 in the section on Probable Errors does not lead us to expect *a priori* any correlation between degree of association and degree of defectiveness, and we must therefore demand pretty clear proof of the existence of such an empirical relation. The facts shown below that women are at once less defective and more highly associated than men, and that partial coefficients of association in undefective universes are higher than total coefficients, and much higher than partial coefficients in defective universes (Tables IV. and V, pp. 306-307), may be said to bring some support to such a hypo-

thesis, but other explanations are here possible. The fact that the association decreases throughout life, as far as we can judge from present material, while defectiveness also decreases in later childhood (*cf.* below, p. 310) is against it. Thus I do not think we can accept the hypothesis without wider evidence; I have mentioned it as it occurred to me, and would probably occur to others, as covering certain of the facts presented.

§ 58. The foregoing figures of Tables I.-III. show that all the defects dealt with by Dr. WARNER are associated to a high degree, though this degree varies somewhat in different groups of material. The question now arises, can we investigate further the nature of the association between A and B or B and C? Suppose the hypothesis to be put forward, for example, that low nutrition was the cause of both defects in development and nerve signs, and that we only found the latter occurring together because they were both generally present in cases of low nutrition; could this hypothesis be tested? It could be proved at once by forming the partial coefficient $|AB|\gamma|$. If this were small the hypothesis would be confirmed, as we would be shown that on excluding all cases of C, A and B ceased to be associated. If, on the other hand, $|AB|\gamma|$ were still large, even though slightly smaller than $|AB|$, the hypothesis could only be partially true or be a partial explanation.

The partial coefficients in undefective or negative universes thus play the same sort of part in checking interpretations as partial coefficients of correlation. Partial associations in positive or mixed universes give further information; if, for instance, $|AB|C|$, $|AB|D|$, $|AB|CD|$, &c., be all of the same order of magnitude as $|AB|$, it is evident that the presence of B continues to be a bad symptom—to render A more likely—even when C, D, &c., are already present. If, on the other hand, these associations are small, or zero within the limits of probable error, the piling up of symptom on symptom, or defect on defect, ceases to make the case any worse.

§ 59. Now in the present case we have four defects to handle. These give 6 total coefficients; 12 first-order coefficients with negative and 12 with positive universes; 6 second-order coefficients with wholly negative, 12 with partially positive, and 6 with wholly positive universes—or 54 altogether (excluding what I have called “group coefficients”). I did not think it worth while to calculate all these, and have confined myself to the total and second-order partial coefficients. These are given in Table IV. for boys and Table V. for girls. As well as working out the associations for children of all ages, I have divided each sex into three groups: Infants, Standards I. to III., and Standards IV. to Extra VII. (material in Report, Table 21). This serves for two purposes: first, to check signs, &c., as given in the “all ages” column; secondly, to give some idea of change of association with age, a purpose for which no other material is available in the Report.*

* A table is given (Table 22 of the Report) showing the frequency of defective groups, but the number of undefective children ($\alpha\beta\gamma\delta$) is not given, nor the number of children observed at each age. This makes the figures useless for discussing the associations of defects in normal children. The importance of the

§ 60. Comparing first the partial coefficients with negative universes, $|AB|\gamma\delta|$, &c., with the total coefficients, we see that in every case, without exception, the partial coefficient is greater than the total. Hence it cannot be true that any one of the defects noted is, or is even indicative of, a *necessary* connecting link between any other two. That low nutrition brings on at once development defects and nerve signs, or development defects and dulness, so that we find these pairs associated is, for instance, a hypothesis that may be partly true but is insufficient to explain the facts observed. Dr. WARNER's hypothesis that "the connecting link between defects of body and defective mental action is the coincident defect of brain which may be known by observation of 'abnormal nerve-signs'"* seems to me equally untenable; it may be so in some cases, but on the other hand the "connecting link" may be a defect of brain *not* indicated by abnormal nerve signs, or not a defect of brain at all. The demonstration of a necessary connecting link X between A and B would, it seems to me, only be complete when $|AB|\xi|$ was shown to be small compared with $|AB|$; the demonstration that *either* X_1 or X_2 or X_3 or X_n had to be present as a connecting link would only be complete if $|AB|\xi_1 \xi_2 \xi_3 \dots \xi_n|$ were shown to be small (zero within the limits of error). Now $|AB|\gamma\delta|$, $|AC|\beta\delta|$, &c., are not small but even larger than $|AB|$, $|AC|$, &c., hence CD, BD, &c., cannot be *necessary* even as alternative connecting links or symptoms of such links in the way described above; the case must be much more complex and depend on a much greater variety of conditions than those described by the four classes of defects noted. The following figures show further how little the absence of nerve signs affects the chance of an individual with development defects being mentally dull; on Dr. WARNER's hypothesis $(A\beta D)/(A\beta)$ should be small compared with $(AD)/(A)$:—

	Boys.	Girls.
Chance of individual being dull who exhibits development defects = $(AD)/(A)$	·385	·449
Ditto, but no nerve signs = $(A\beta D)/(A\beta)$	·341	·411
Ditto, but neither nerve signs nor low nutrition = $(A\beta\gamma D)/(A\beta\gamma)$	·329	·414

§ 61. Turning next to the partial coefficients with wholly or partly defective universes (*i.e.*, associations in groups of which every member possesses either one or two defects in addition to the possible two of which the associations are considered), we see that the great majority are small and many even negative. The probable errors are, however, high, since the material is small when we are confined to those who are defective, so one cannot always lay great stress on the sign. In three cases

omission is apparently unrecognised, as the last Report issued (1899) only gives more such figures; this seems to me waste of time and money.

* Report, p. 13.

TABLE IV.—Showing the Associations between Defects for Boys, for different Groups of Standards, and for all Ages together. (1892-94 investigation.)

A. Development Defects. B. Nerve Signs. C. Low Nutrition. D. Mental Dulness.

Coefficient of association.	Infants.	Standards I.-III.	Standards IV.- Ex. VII.	All ages.*
AB	+·794 ± ·014	+·743 ± ·010	+·722 ± ·016	+·750 ± ·005
AC	+·900 ± ·009	+·816 ± ·013	+·802 ± ·025	+·848 ± ·007
AD	+·880 ± ·008	+·834 ± ·007	+·822 ± ·013	+·846 ± ·005
BC	+·862 ± ·012	+·749 ± ·016	+·845 ± ·019	+·783 ± ·010
BD	+·928 ± ·005	+·890 ± ·005	+·886 ± ·008	+·897 ± ·003
CD	+·868 ± ·011	+·792 ± ·014	+·748 ± ·034	+·823 ± ·008
AB $\gamma\delta$	+·859 ± ·016	+·827 ± ·010	+·790 ± ·016	+·826 ± ·007
AC $\beta\delta$	+·962 ± ·006	+·928 ± ·009	+·928 ± ·016	+·942 ± ·005
AD $\beta\gamma$	+·947 ± ·006	+·937 ± ·005	+·933 ± ·008	+·939 ± ·003
BC $\alpha\delta$	+·948 ± ·010	+·896 ± ·013	+·935 ± ·015	+·912 ± ·008
BD $\alpha\gamma$	+·973 ± ·003	+·951 ± ·003	+·946 ± ·005	+·955 ± ·002
CD $\alpha\beta$	+·964 ± ·007	+·935 ± ·011	+·923 ± ·026	+·949 ± ·006
AB γD	-·429 ± ·060	-·421 ± ·038	-·532 ± ·068	-·443 ± ·027
AB $C\delta$	-·227 ± ·112	-·335 ± ·089	-·486 ± ·126	-·348 ± ·059
AC βD	+·013 ± ·101	+·125 ± ·088	+·025 ± ·211	+·096 ± ·060
AC $B\delta$	+·418 ± ·090	+·116 ± ·079	+·043 ± ·124	+·210 ± ·053
AD βC	-·149 ± ·111	+·193 ± ·101	+·062 ± ·233	+·076 ± ·070
AD $B\gamma$	+·055 ± ·079	+·088 ± ·039	+·018 ± ·065	+·079 ± ·030
BC αD	-·066 ± ·102	-·227 ± ·083	-·034 ± ·187	-·201 ± ·057
BC $A\delta$	+·286 ± ·087	-·077 ± ·082	+·098 ± ·133	-·002 ± ·054
BD αC	+·251 ± ·118	+·159 ± ·102	+·062 ± ·210	+·140 ± ·070
BD $A\gamma$	+·370 ± ·066	+·211 ± ·043	+·132 ± ·069	+·226 ± ·031
CD αB	+·116 ± ·100	+·014 ± ·071	-·126 ± ·126	+·077 ± ·050
CD $A\beta$	+·043 ± ·085	+·174 ± ·073	-·012 ± ·165	+·160 ± ·049
AB CD	-·223 ± ·120	-·211 ± ·105	-·263 ± ·245	-·233 ± ·072
AC BD	+·239 ± ·100	+·345 ± ·069	+·335 ± ·155	+·323 ± ·051
AD BC	-·137 ± ·128	+·318 ± ·094	+·312 ± ·184	+·197 ± ·044
BC AD	+·164 ± ·103	+·003 ± ·080	+·281 ± ·181	+·035 ± ·058
BD AC	+·255 ± ·111	+·286 ± ·097	+·312 ± ·206	+·254 ± ·067
CD AB	-·088 ± ·113	+·251 ± ·081	+·176 ± ·167	+·197 ± ·058
Per cent. with A . . .	7·9	9·9	7·4	8·8
" " B . . .	6·3	13·5	8·3	10·9
" " C . . .	3·7	3·1	1·5	2·8
" " D . . .	6·7	9·7	5·4	7·9
" " any defect	14·0	21·2	16·3	18·2
Number observed . .	7,055	11,482	7,168	26,287

* "All ages" includes those in Standard 0 and in no Standard not included in the other columns.

TABLE V.—Showing the Associations between Defects for Girls, for different Groups of Standards, and for all Ages together. (1892-94 investigation.)

A. Development Defects. B. Nerve Signs. C. Low Nutrition. D. Mental Dulness.

Coefficient of association.	Infants.	Standards I.-III.	Standards IV.- Ex. VII.	All ages.*
AB	+·850 ± ·013	+·795 ± ·010	+·747 ± ·021	+·784 ± ·008
AC	+·949 ± ·005	+·903 ± ·007	+·881 ± ·015	+·916 ± ·004
AD	+·927 ± ·006	+·886 ± ·006	+·898 ± ·010	+·900 ± ·004
BC	+·866 ± ·013	+·821 ± ·013	+·821 ± ·021	+·814 ± ·009
BD	+·935 ± ·006	+·908 ± ·005	+·880 ± ·010	+·905 ± ·004
CD	+·876 ± ·012	+·833 ± ·011	+·746 ± ·034	+·835 ± ·008
AB $\gamma\delta$	+·896 ± ·016	+·881 ± ·009	+·783 ± ·026	+·850 ± ·009
AC $\beta\delta$	+·970 ± ·004	+·974 ± ·004	+·955 ± ·009	+·971 ± ·002
AD $\beta\gamma$	+·960 ± ·005	+·957 ± ·004	+·963 ± ·005	+·959 ± ·003
BC $\alpha\delta$	+·957 ± ·009	+·940 ± ·008	+·897 ± ·017	+·927 ± ·007
BD $\alpha\gamma$	+·980 ± ·003	+·956 ± ·003	+·932 ± ·008	+·955 ± ·002
CD $\alpha\beta$	+·940 ± ·014	+·941 ± ·010	+·936 ± ·016	+·941 ± ·007
AB γD	-·381 ± ·077	-·363 ± ·045	-·437 ± ·076	-·394 ± ·033
AB $C\delta$	-·200 ± ·123	-·432 ± ·079	-·175 ± ·140	-·352 ± ·057
AC βD	+·445 ± ·099	+·394 ± ·076	-·172 ± ·180	+·325 ± ·056
AC $B\delta$	+·422 ± ·108	+·315 ± ·071	+·571 ± ·081	+·445 ± ·045
AD βC	+·308 ± ·117	+·155 ± ·102	-·070 ± ·199	+·170 ± ·068
AD $B\gamma$	+·090 ± ·101	+·147 ± ·048	+·433 ± ·072	+·257 ± ·035
BC αD	-·061 ± ·154	+·006 ± ·090	-·347 ± ·149	-·108 ± ·065
BC $A\delta$	+·246 ± ·097	-·106 ± ·079	+·223 ± ·126	+·011 ± ·055
BD αC	+·320 ± ·139	+·156 ± ·105	-·144 ± ·178	+·143 ± ·077
BD $A\gamma$	+·418 ± ·076	+·127 ± ·055	+·152 ± ·097	+·211 ± ·039
CD αB	-·222 ± ·135	+·015 ± ·071	-·117 ± ·120	+·012 ± ·055
CD $A\beta$	+·115 ± ·077	-·007 ± ·072	-·339 ± ·149	-·019 ± ·049
AB CD	-·275 ± ·185	-·376 ± ·092	-·091 ± ·268	-·296 ± ·072
AC BD	+·535 ± ·101	+·381 ± ·067	+·200 ± ·209	+·421 ± ·051
AD BC	+·234 ± ·155	+·219 ± ·105	+·016 ± ·232	+·230 ± ·071
BC AD	+·058 ± ·107	-·010 ± ·079	+·015 ± ·230	+·006 ± ·058
BD AC	+·247 ± ·110	+·220 ± ·092	+·016 ± ·232	+·230 ± ·071
CD AB	-·078 ± ·126	+·089 ± ·085	-·511 ± ·152	-·027 ± ·063
Per cent. with A . .	7·8	7·3	4·2	6·8
" " B . .	4·2	10·3	8·8	8·5
" " C . .	3·9	3·4	2·0	3·2
" " D . .	5·3	8·3	4·5	6·9
" " any defect . .	11·8	16·6	13·2	14·8
Number observed . .	6,274	11,090	6,026	23,713

* "All ages" includes those in Standard 0 and in no Standard not included in the other columns.

at least, however, if not in four, the negative sign appears to be certainly significant; I refer to the partial associations of A and B $|AB|\gamma D|$, $|AB|C\delta|$, and $|AB|CD|$, in which cases all the twenty-four coefficients for both sexes are negative: and the one partial coefficient $|BC|aD|$, seven out of the eight examples of which are negative, the one positive value (Girls, Standards I.-III.) being only 1/15th of its probable error. The first case is the most general and remarkable, but in both it will be noted we are dealing with an association of nerve signs. As might be conjectured from the generality of the sign, $|AB|C|$ and $|AB|D|$ are also negative, *i.e.*, when individuals exhibit either low nutrition or mental dulness, or both, the presence of nerve signs lessens the probability of development defects being present and *vice versa*.

This case is most remarkable, and the following figures, showing the chance of an individual exhibiting development defects (or nerve signs) when he exhibits nerve signs (or development defects), and so on, illustrate it further. Multiplied by 100 the chances can, of course, be read as percentages, *i.e.*, 50 per cent. of C's are A, but only 42 per cent. of BC's are A (for the boys), and so on.

A. Development Defects. B. Nerve Signs. C. Low Nutrition. D. Dulness.

Chance of individual—			Chance of individual—		
Who is	being A.		Who is	being B.	
	Boys.	Girls.		Boys.	Girls.
B	·311	·291	A	·384	·363
C	·499	·556	C	·471	·435
D	·428	·445	D	·576	·526
BC	·423	·466	AC	·398	·364
BD	·337	·352	AD	·454	·417
CD	·529	·606	CD	·523	·478
BCD	·473	·530	ACD	·468	·418

In every case the presence of B is antagonistic to that of A when either C or D is present; and A is similarly antagonistic to B. I am quite unable to suggest any possible explanation of this, but so unexpected a result ought to throw some light on the physiological relations between the signs observed. It is particularly curious to note that A and B are negatively associated in the presence of either of two defects so apparently different as mental dulness and low nutrition. The point seems to be worth further investigation by the committee.*

* Note 4/4/00.—Dr. E. B. SHULDHAM writes to me as follows: "My experience with boys at the Bisley farm schools was that many of the boys who had left poor homes in London with insufficient feeding suffered from suppuration of the cervical glands a few weeks after their removal to Bisley, also to a great change for the better in food, clothing, and shelter. After a prolonged residence at Bisley the glandular enlargements lessened, and the suppuration ceased." This is interesting for comparison with the above, as we have here

Change of Association with Age.

§ 62. I gather from Table XXV. of the Report that the average age of the "Infants" would be three or four years, Standards I.-III. about seven years, and Standards IV.-Ex. VII. eleven or twelve. It is unsatisfactory not having a clear classification of the children by age pure and simple, as a classification of Standards must imply an uncertain amount of selection by mental capacity.

It is a curious point that Standards I.-III. exhibit a higher percentage of defects, with the exception of cases of low nutrition, than either the "Infants" or Standards IV.-Ex. VII. The percentages are given in full for each separate Standard in Table VI. below, and in every defect there is a rise in frequency on passing from the

TABLE VI.—Showing the percentages of Children with given Defects and with any Defect in the different Standards. (1892-94 investigation.)

A. Development Defects. B. Nerve Signs. C. Low Nutrition. D. Mental Dulness.

	Nominal age.	Boys.					Girls.				
		A	B	C	D	With any defect.	A	B	C	D	With any defect.
Infants	0-5	7.9	6.3	3.7	6.7	14.0	7.8	4.2	3.9	5.3	11.8
Standard I.	6	11.5	13.9	4.1	11.0	22.9	8.4	10.6	4.7	9.5	17.2
" II.	7	9.7	14.1	2.9	9.2	21.2	7.2	10.3	3.2	8.1	17.1
" III.	8	8.2	12.4	2.0	8.6	19.3	6.0	10.0	2.2	7.1	15.3
" IV.	9	7.5	11.8	1.6	7.0	17.9	4.5	9.3	2.1	5.6	13.7
" V.	10	7.7	9.7	1.2	4.9	16.2	4.7	7.7	1.8	2.1	12.7
" VI.	11	7.4	9.0	1.7	4.3	15.6	3.0	9.9	2.2	3.5	13.6
" VII.	12	6.5	7.0	1.2	2.8	12.4	2.5	8.6	2.3	1.6	11.9
" Ex. VII.	13	5.5	6.9	2.1	2.8	11.8	3.8	6.9	1.5	3.8	10.7
All ages		8.8	10.9	2.8	7.9	18.17	6.8	8.5	3.2	6.9	14.78

"All ages" includes those in Standard 0 and in no Standard.

group of "Infants" to Standard I.—in most cases a considerable rise, the percentages of nerve signs more than doubling, and the percentages of development defects for

an apparently negative association between "suppuration" and "low nutrition" in the case of boys of poor physique. Dr. SHULDHAM also states that the late Mr. H. JONES, for many years Superintendent of the boys at Bisley, noticed the fact that those boys who did not take green vegetables with their food suffered from night-blindness, which ceased when he insisted on their taking green food regularly for some weeks. This suggests that further inquiry as to nutrition and eyesight might be of a good deal of interest.

boys increasing by half; the percentage of dull also increases largely. One can only conclude that these defects, whether inherited or not, are not "innate" in the simple sense of being observable at birth or during early infancy; possibly they may be brought on in part by the school attendance itself, a theory which would account for the sudden rise after "Infancy," or rather early childhood. As for the subsequent decreases in the percentages of all defects, I am inclined to attribute them, in part at all events, to the selection by capacity that must take place. This would reduce the percentage of "mentally dull," and, owing to the association between defects, would also reduce indirectly the percentages of those with other defects. A proportion of the decrease one would expect to take place from natural selection, but probably a small proportion. We have, in fact, selective mortality, selection by mental capacity, and growth (change in the individual), all acting together as causes of change—and very probably also initial differences between the groups from which the older and younger children sprang—precisely as was indicated in the previous discussion on pp. 299–300.

§ 63. In the association coefficients there is, however, no irregularity in the group Standards I.–III.; the most cursory inspection of Tables IV. and V. shows that the total coefficients and partial coefficients with negative universes decrease when we pass from "Infants" to the next group, and again from Standards I.–III. to the next group. The changes in partial associations with positive or defective universes are not so obvious, partly, no doubt, because these coefficients are small and have large probable errors, but the majority of the changes are in the same direction. Table VII. shows the total number of changes in either direction. Thus comparing Standards I.–III. with "Infants," we see that in the case of the boys all the total associations and all the partials with negative universes have decreased; of the partial associations in defective universes 8 only decreased while 10 have increased. Taking all cases together there are 88 decreases to 32 increases, but if we cut out the partials 22 decreases to 2 increases only. However we take it there is overwhelming evidence that association in general decreases as age advances.

§ 64. That this is a law of pretty general application seems to be borne out by the entirely different class of statistics drawn from the English Census.* In Table VIII. are given the associations derived from these figures between blindness and dumbness, blindness and mental derangement, and dumbness and mental derangement. The figures do not run quite regularly, but the associations for the age group 5–15 are, in every case, greater than the "all-ages" associations, and if we draw curves showing the change of association during life the downward trend is quite obvious (curves of figs. 1, 2, 3, p. 314).

Such decrease is again not, of course, the result of selection alone but of selective mortality, growth (change in the individual), and initial differences in the child-populations from which the successive age groups were formed. That changes in the

* *Loc. cit.*, on p. 42.

individual will decrease association is obvious in the case of such a defect as blindness, which may be brought on by accident, cataract, or other causes having no bearing on mental derangement or dumbness. It is not obvious, however, why the association between blindness and mental derangement should be much smaller than the association between blindness and dumbness in the later age groups.

§ 65. The question of what would be the effect of selection alone—or whether it would have any regular effect in one direction—is, however, a most interesting one.

TABLE VII.—Showing the Number of Cases in which the Association Coefficient decreased or increased on passing from one group of Standards to the next. There is a great majority of decreases.

Class of coefficient.	Boys.				Girls.				Total.	
	Infants to Standards I.-III. Association.		Standards I.-III. to IV.-VII. Association.		Infants to Standards I.-III. Association.		Standards I.-III. to IV.-VII. Association.		Association.	
	Decrease.	Increase.	Decrease.	Increase.	Decrease.	Increase.	Decrease.	Increase.	Decrease.	Increase.
Total coefficients	6	—	5	1	6	—	5	1	22	2
Universe with no other defect	6	—	5	1	4	2	5	1	20	4
Universe defective	8	10	14	4	13	5	11	7	46	26
Total . . .	20	10	24	5	23	7	21	9	88	32

(Note.—Two coefficients that remained constant from one Standard group to the next have been entered as decreasing.)

The fact that partial associations in undefective universes are higher than total associations, combined with my first impression (unjustified I think) that associations were, on the whole, higher in the healthier groups, led me at first to believe that the effect of selection would be to increase associations. I still cannot help thinking that this is practically, as it is formally, possible, it being remembered that association will decrease or increase simply according as

$$s_1 s_3 \leq s_2 s_4,$$

$s_1 s_2 s_3 s_4$ being the survival rates in the four classes AB, A β , &c. (*vide* § 54).

§ 66. We have no material, as already stated, for testing the effect of pure selection with any absolute certainty. The greater number of the deaf and dumb, however, possess their defect from birth or early childhood, and the same statement holds good for imbeciles or idiots as distinct from the insane. Hence the association between deaf-mutism and imbecility will be affected by selection (selective mortality) to a large extent, at all events, as compared with those associations that were given in Table VIII. The necessary data for discussing the association in this case are given in the English Census for 1881 (*loc. cit.*, note on p. 298), and the results are tabulated in Table IX. The figures for males show a steady and continuous decrease in association, without a break; for females there is, on the whole, a decrease, but it is less regular.* Taking both sexes together, I think the decrease in association is rather greater for dumbness and imbecility than for dumbness and mental derangement. Thus Table IX. seems to point to selection causing *decrease* of association. This is the only evidence we have of at all a direct character, and so its results should be accepted pending the production of anything better. At the same time the material is obviously not unimpeachable, and an endeavour should be made to get reliable statistics for the special purpose.†

Differences between the Sexes.

§ 67. The differences exhibited by the sexes as regards association are so marked that they can hardly have failed to have struck the reader of the foregoing tables. In an immense majority of cases the association is greater for females than for males—dealing only with the total associations that is to say.‡ This is true for all divisions of one material, and for the Census defects as well as for those dealt with by Dr. WARNER. The evidence is collected in Table X., which is based entirely on the preceding tables. In 87 cases out of 101, or 86 per cent., the associations are greater for females than for males. There seems some indication of a decrease in the difference with advancing age; thus in Standards IV.—Ex. VII. the females are only greatest in 3 cases of 6. In the age groups over 25, pooling Tables VII. and IX. together, the females only exceed in 71 per cent. of the cases, or 15 out of 21, instead of 86 per cent., or 18 out of 21.

§ 68. Besides being more highly associated, women are also in general less defective than men. They exhibit a smaller percentage of individuals with development defects, nerve signs, or mental dulness, but a slightly higher percentage with low

* It will be noted that the age groups are not the same as in the last case, the figures being grouped more coarsely in the 1881 Census.

† Professor PEARSON informs me that unpublished material in his hands goes to show that correlation decreases with age; theoretically also he would expect selection to decrease correlation.

‡ This is again in accord with the evidence for correlation—females being more highly correlated than males.

TABLE VIII.—Showing the Associations between Blindness, Deaf-mutism, and Mental Derangement for both Sexes and different Age Groups; and the proportion per 100,000 of Deaf, Dumb, and Mentally Deranged. (Census of England and Wales, 1891.)

The sign of the association is +, if not entered.

All ages.		5—	15—	25—	35—	45—	55—	65—	75—.		
Association between	{ Blindness and dumb- ness	Male	.769 ± .019	.893 ± .022	.792 ± .051	.866 ± .028	.625 ± .103	.747 ± .057	.697 ± .072	.597 ± .109	.698 ± .089
		Female	.842 ± .013	.937 ± .013	.796 ± .062	.859 ± .040	.886 ± .026	.890 ± .024	.835 ± .024	.701 ± .078	.662 ± .087
	{ Blindness and mental derangement	Male	.648 ± .015	.921 ± .013	.753 ± .034	.607 ± .049	.572 ± .041	.459 ± .048	.412 ± .049	.198 ± .070	-.126 ± .111
		Female	.708 ± .011	.950 ± .008	.769 ± .040	.786 ± .026	.622 ± .042	.579 ± .039	.572 ± .036	.342 ± .047	.019 ± .068
	{ Mental derangement and dumbness	Male	.853 ± .005	.912 ± .008	.804 ± .020	.866 ± .011	.789 ± .019	.823 ± .017	.815 ± .021	.797 ± .033	.622 ± .148
		Female	.826 ± .007	.931 ± .009	.846 ± .017	.828 ± .017	.800 ± .019	.746 ± .027	.752 ± .031	.802 ± .030	.808 ± .043
Proportion per 100,000 of popula- tion in same age group	{ Blind . . .	Male	87	26	44	56	93	147	247	435	1051
		Female	75	22	32	37	58	113	186	396	1119
	{ Dumb . . .	Male	55	68	59	56	62	58	57	53	44
		Female	43	50	49	45	50	46	45	42	43
	{ Deranged . . .	Male	323	85	229	246	572	687	753	769	679
		Female	348	62	173	376	602	806	906	946	976

Diagrams Illustrating the Change in Association of Defects during Life (Table VIII.).

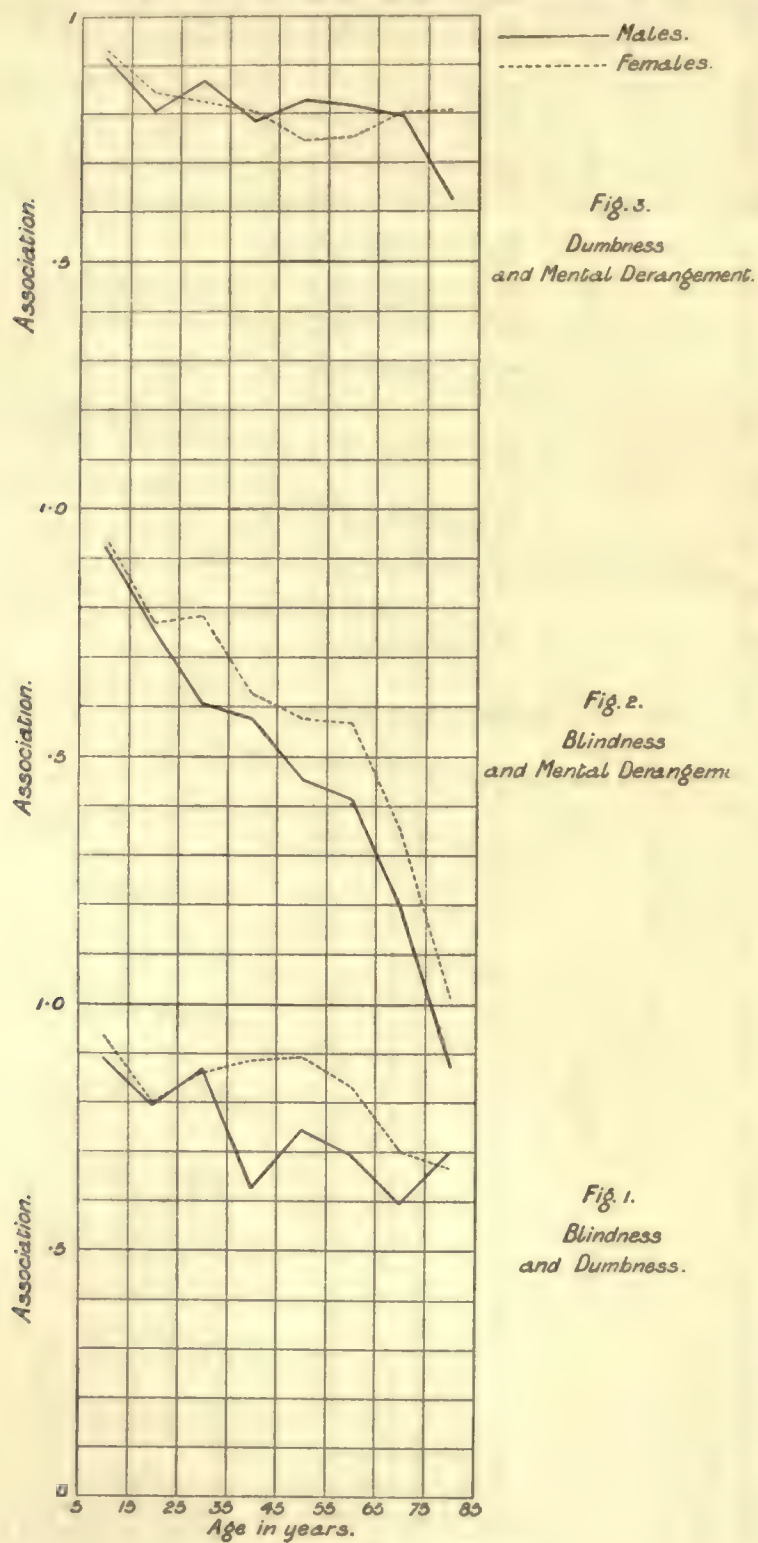


TABLE IX.—Showing the Association between Imbecility or Idiocy and Deaf-mutism for both Sexes and successive Age Groups; and the proportion per 100,000 of Imbeciles and Deaf-mutes.

			All ages.	5—	15—	25—	45—	65—
Association between imbecility and dumbness. . . }		Male	·924 ± ·003	·943 ± ·005	·931 ± ·006	·907 ± ·008	·889 ± ·014	·482 ± ·184
		Female	·913 ± ·004	·953 ± ·005	·878 ± ·015	·890 ± ·010	·910 ± ·010	·770 ± ·053
Proportion per 100,000 in same age group.	Deaf and dumb }	Male	56	63	65	63	61	61
		Female	46	55	51	52	47	52
	Imbeciles or idiots }	Male	128	97	174	156	149	217
		Female	125	67	136	161	186	273

nutrition.* In the case of Census defects (Tables VIII. and IX.), the proportion per 100,000 living at all ages is less for females in blindness, deaf-mutism, and imbecility, but greater for females in the case of general mental derangement. Comparing the separate age groups the proportion per 100,000 living at each age is least for females in every case at age groups under twenty-five. In the older age groups, on the other hand, in the cases of mental derangement and imbecility, the females show the greater proportion of defectives.

Thus at first sight it would appear that the female, though at first a greatly superior animal to the male, was liable to break down mentally at a much more rapid rate and at an earlier age. This, however, would probably be a fallacious conclusion; it is pointed out in the Census Report for 1881 that the death-rate for male lunatics is known to be very much higher than for female lunatics—almost half as high again in fact.† Hence the greater proportion per 1000 living at the later age groups may, either entirely or to a large extent, be simply due to accumulation. There is apparently no evidence that the *case-rate* is greater for females at the higher age groups. Thus, so far as we can say at present, the female may remain the less defective animal throughout life.

§ 69. Summarising the general conclusions, I have shown good ground for accepting as general laws that females are more highly associated than males, and that

* Cf. Table VI., p. 54, for a comparison in each separate Standard.

† General Report for 1881, pp. 66–67 :—“According to the returns of the Lunacy Commissioners from 1872 to 1881 inclusively, the mean annual death-rate among the registered male insane was 11·94 per cent. of the average daily number on the register, while the death-rate of the females was 8·13 per cent. The recovery rate of the males was 10·50 per cent., and that of the females 11·59 per cent.”

TABLE X.—Showing the number of Cases in which the Association between Defects is greater for Males and greater for Females (based on preceding tables).

* Number of cases in which the association is greater.	Table I.		Table II.				Table III.		
	1888-1891.	1892-1894.	Certified industrial schools.	Poor Law schools.	Homes and orphanages.	Public elementary.	English.	Jews.	Irish.
For males	—	—	1	1	1	—	1	—	—
For females	6	6	5	5	5	6	5	6	6

* Number of cases in which the association is greater.	Tables IV. and V.			Table VIII.			Table IX.		Total.
	Infants.	Standards I.-III.	Standards IV.-VII.	5-25	25-45	45-.	5-25	25-.	
For males	—	—	3	—	2	3	1	1	14
For females	6	6	3	6	4	9	1	2	87

* Total associations only.

associations are greater for the young than the old. I have not, however, been able to say with certainty whether the decrease in association was due to growth (change in the individual) aided by selection, or growth opposed by selection. The only available evidence suggested that selection acted in the same direction as growth.

The total associations between defects were always high, except in some cases for the very old, but the partial associations for defective universes were in most cases low, and in some cases even certainly negative. The partial associations for un-defective universes were, on the other hand, higher than the total coefficients, a fact which I held to imply that no one of the defects recorded was necessary as a connecting link between any other pair.

§ 70. During the course of the present investigation I have naturally been led to study pretty thoroughly the "Report" of the Committee on Childhood, and the papers by Dr. WARNER, bearing on the same subject, in the 'Journal of the Royal Statistical Society'—papers which first drew my attention to the need of a theoretical study of the whole subject of association. I may be pardoned, then, for offering some suggestions as to the work of the Committee as regards both the mode

of publication or arrangement of its results, and the directions in which future work might possibly be undertaken.

To deal with the questions of arrangement, &c., first. I suggest that the notation might with great advantage be altered to the notation of JEVONS, such as I have used. The shortcomings of a notation which has to represent the simple second-order frequency $(A\beta)$ by $(A+) - (AB+)$ are obvious. Next, I have noticed that the arrangement of frequencies is very irregular in the report. Where the ultimate fourth-order frequencies (Dr. WARNER'S "Primary" groups) alone are given it is quite clear, but where more are given the data are seldom complete, and groups of the same order are not kept together. As an example of the way in which I think frequencies ought to be given I append a table giving the general results of the 1892-94 investigation. If so much space could not be spared, I think the statement of the fourth-order frequencies is quite sufficient, as the others can be so readily calculated from them.*

As regards future work, I find myself unable to follow at all the remarks made by the Committee on p. 5 of the "Report" (the italics are mine):—

"A very valuable addendum to vital statistics might be obtained by following up the history of certain cases recorded, by subsequent periodical inspections, but *as this is beyond the power of the present Committee*, it can only be suggested as one among many other directions in which enquiry may be pushed in the hands of official Commissions."

The Committee—or Childhood Society—is, as I gather from its Reports, continuing the work of inspecting children in schools, and why it should be "beyond their power" to reinspect a few large schools year by year is by no means obvious. They are at present (in the last Reports,† for 1898-99) issuing statistics of the frequencies of different groups of defects for different ages. As I have already pointed out (note on p. 304) these statistics are rendered almost worthless by the omission of the frequency $(\alpha\beta\gamma\delta)$ —the number of *undefective* children—at each age, only those who were defective having apparently been noted. Even if the material were, however, complete, it would not enable us to distinguish between changes due to selection and changes due to growth, nor consequently to state what are the effects of these agencies each by itself. Nothing but observance of one group of individuals year by year can do this, and there seems little more difficulty in this than in the work already being carried out. It is surely futile to expect a Royal Commission on the subject. It would, in fact, be more appropriate for a body, specially created for the "Scientific Study" of childhood, to take up an investigation of the greatest scientific interest but probably of little immediate practical use. I would most strongly urge the

* There appear to be a good many misprints in the Report, many of the frequencies being in disagreement with those given for the ultimate ("Primary") groups. I have generally assumed the "primary" frequencies to be correct.

† British Association Reports, 1898, p. 691; 1899, p. 489.

TABLE showing the Frequencies of all Groups of Defects. All Ages.
(1892-94 investigation.)

Group.	Frequency.		Group.	Frequency.		Group.	Frequency.	
	Boys.	Girls.		Boys.	Girls.		Boys.	Girls.
$\alpha\beta\gamma\delta$	21,511	20,207	$\alpha\beta\gamma$	21,842	20,504	$\alpha\beta$	22,013	20,667
$A\beta\gamma\delta$	802	445	$\alpha\beta\delta$	21,619	20,317	$\alpha\gamma$	23,604	21,753
$\alpha B\gamma\delta$	1,059	762	$\alpha\gamma\delta$	22,570	20,969	$\alpha\delta$	22,793	21,188
$\alpha\beta C\delta$	108	110	$\beta\gamma\delta$	22,313	20,652	$\beta\gamma$	23,038	21,263
$\alpha\beta\gamma D$	331	297	$A\beta\gamma$	1,196	759	$\beta\delta$	22,555	20,924
$AB\gamma\delta$	415	207	$A\beta\delta$	936	607	$\gamma\delta$	23,787	21,621
$A\beta C\delta$	134	162	$A\gamma\delta$	1,217	652	$A\beta$	1,421	1,031
$A\beta\gamma D$	394	314	$B\gamma\delta$	1,474	969	$A\gamma$	1,934	1,190
$\alpha BC\delta$	115	109	$\alpha B\gamma$	1,762	1,249	$A\delta$	1,420	891
$\alpha B\gamma D$	703	487	$\alpha B\delta$	1,174	871	αB	1,966	1,428
$\alpha\beta CD$	63	53	$\alpha\beta C$	171	163	$B\gamma$	2,500	1,680
$ABC\delta$	69	77	$\alpha C\delta$	223	219	$B\delta$	1,658	1,155
$AB\gamma D$	323	224	$\beta C\delta$	242	272	αC	375	342
$A\beta CD$	91	110	$\alpha\beta D$	394	350	βC	396	435
αBCD	89	70	$\beta\gamma D$	725	611	$C\delta$	426	458
$ABCD$	80	79	$\alpha\gamma D$	1,034	784	αD	1,186	907
Total .	26,287	23,713	$AB\gamma$	738	431	βD	879	774
			$AB\delta$	484	284	γD	1,751	1,322
			$A\beta C$	225	272	AB	887	587
			$AC\delta$	203	239	AC	374	428
			$A\beta D$	485	424	AD	888	727
			$A\gamma D$	717	538	BC	353	335
			αBC	204	179	BD	1,195	860
			$BC\delta$	184	186	CD	323	312
			$B\gamma D$	1,026	711			
			αBD	792	557	A	2,308	1,618
			αCD	152	123	α	23,979	22,095
			βCD	154	163	B	2,853	2,015
			ABC	149	156	β	23,434	21,698
			ABD	403	303	C	749	770
			ACD	471	189	γ	25,538	22,943
			BCD	169	149	D	2,074	1,634
						δ	24,213	22,079
						Total .	26,287	23,713

importance of such reinspections of the same children on the Childhood Society and the Committee of the British Association that corresponds with it.

As a further subject, I suggest the question as to the hereditary character of these defects—development defects, nerve signs, low nutrition, and mental dulness—not necessarily by studying the parents, which would probably be a difficult matter, but by noting pairs of brothers. Suppose a large number of groups of brothers*—"fraternities"—to be noted for some defect, say A; reckon for each

* Or, of course, sisters; or brothers and sisters, "geschwister," "siblings" as Professor PEARSON has proposed to call them, since we have no modern English word for members of the same family without regard to sex.

fraternity the number of AA, Aa, aA, and aa pairs, as in the example on "Temper in Fraternities," p. 291, and tabulate the total number of such separate pairs as in that example. These numbers give the association between brothers at once.

A certain portion of such fraternal association might be due to similarity of environment for the brothers, if the defects observed were much affected by this. I do not see how the home-environment could be allowed for, but it could be tested whether the environment of school had any such effect. Take from a considerable number—say 100—different schools a series of samples, say 50 or 100 children from each. Each of these groups forms what we may call a "community" or group subjected to common conditions, as opposed to the fraternity. Find the association between members of the Community in just the same way as the association between members of the Fraternity. This would give a measure of the effect of environment as opposed to inheritance. Possibly this might be done with the material now in the hands of the Society.

VIII. *The Ionization of Dilute Solutions at the Freezing Point.**By* W. C. D. WHETHAM, M.A., *Fellow of Trinity College, Cambridge.**Communicated by* E. H. GRIFFITHS, F.R.S.

Received February 14,—Read February 22, 1900.

INTRODUCTION.

THE existence of a relation between the depression of the freezing point, produced by dissolving an acid or a salt in water, and the electrolytic conductivity of the solution thus obtained was pointed out by ARRHENIUS in 1887, and has been the subject of much experiment and discussion since that date.

As is well known, the facts of electrolysis indicate that an electric current, when passing through a solution, is associated with a passage in opposite directions of the constituents of the salt. FARADAY called these mobile parts ions. The number of the ions depends on the chemical nature of the salt, and is usually indicated by its formula. Thus for one molecule of potassium chloride we have two ions, the potassium travelling in one direction and the chlorine in the other. For barium chloride or sulphuric acid we have three ions, and, since the electric charge of an ion is proportional to its valency, the electrically equivalent weights of these substances are represented by $\frac{1}{2}\text{BaCl}_2$ and $\frac{1}{2}\text{H}_2\text{SO}_4$, respectively.

The freezing point of water is depressed by equal amounts when molecularly equivalent weights of various non-electrolytes, such as cane-sugar or alcohol, are dissolved in it. Equivalent quantities of electrolytes, however, produce greater effects. Thus a gramme-molecule of potassium chloride causes nearly twice as much depression as a gramme-molecule of sugar, while the effect of barium chloride or sulphuric acid is almost three times as great as that of a non-electrolyte. It will be noticed that the molecular depression of the freezing point is approximately proportional to the number of ions into which we must suppose the salt resolved in order to explain its electrical properties.

Again, if the concentration of a solution be diminished by continual dilution, it is found that the conductivity decreases at a slower rate, so that a rise occurs in the value of the equivalent conductivity, a quantity which is defined as the conductivity of the solution divided by its concentration expressed in electrical gramme-equivalents. This rise continues till the dilution has reduced the concentration to a value of about the ten-thousandth of a gramme-equivalent of the solute per litre of solution, after

which the equivalent conductivity reaches a limit. Beyond this point further dilution causes no corresponding rise, and in the case of acids and alkalies eventually leads to a sudden decrease in the equivalent conductivity.

These variations are usually referred to changes in the percentage amount of the dissolved substance which is actively concerned in conveying the electric current, and it is easy to calculate what proportion of the whole quantity of such substance must be active in any given solution, for, if no other condition changes, it is measured by the ratio of the equivalent conductivity of the solution to its maximum value. This ratio is therefore known as the coefficient of ionization.

In examining the freezing point phenomena, very similar variations are noticed. The molecular depression is relatively greater in those solutions where the ionization is complete, or nearly complete, and relatively less where the conductivity shows that more of the salt is electrically inactive.

Whether this relation between the electrical ionization and the depression of freezing point is exact or only approximate is one of the most important questions in the present state of the theory of solution, and, although an enormous amount of experimental work has been devoted to the subject, it is still a question the answer to which remains uncertain.

This uncertainty arises from two causes. The first is the difficulty of determining the extremely small freezing-point depressions of very dilute solutions, and the second is the fact that most of the comparisons have been made with the ionization of solutions measured by KOHLRAUSCH, OSTWALD and others at temperatures of 18° or 25° Centigrade. Now, unless the temperature coefficients of conductivity are the same for different concentrations of a solution, the ionization at 18° will not be the same for a definite concentration as the ionization at 0° , with which it is evident that the freezing point phenomena should be compared.

As far as is known to the present writer, the only measurements of the ionization of electrolytic solutions which have been made at 0° are those of R. W. WOOD.* He finds that the ionization of solutions of potassium chloride, sodium chloride, dichloroacetic acid, and trichloroacetic acid is, as long as the dilution is great, sensibly the same at 0° as it is at 18° , or, at all events, that the difference between the values at these temperatures is not enough to bring the conductivity measurements into harmony with the freezing point values. The observations were only carried to a dilution such that one gramme-equivalent weight would be contained in 1024 litres. This is insufficient to give the limiting values of the molecular conductivity directly, so "the value expressing the conductivity of infinitely dilute solutions was calculated by means of the temperature coefficient from the values found by KOHLRAUSCH and OSTWALD for 18° and 25° ."

Apparently this process must involve a certain amount of extrapolation, for the

* 'Zeitschrift für Phys. Chemie,' vol. 18, p. 3, 1895. Translated in the 'Phil. Mag.,' vol. 41, p. 117, 1896.

temperature coefficients of the conductivity of electrolytes vary greatly, as either the concentration or the temperature is changed. The numbers which follow show this clearly for the case of barium chloride. The measurements were made by determining the conductivity of the solutions between 0° and 18° at intervals of about 2° ; the figures were carefully plotted on a diagram, and the value of the tangent to the curve estimated at several points. The following temperature coefficients were thus obtained :—

Solution I.—Concentration = 0.0004 gramme-equivalent per thousand grammes of solution.

Temperature.	Resistance.	Temperature coefficient per cent.
1°	766.3	3.11
5	680.0	2.89
9	608.5	2.70
13	549.0	2.51
17	498.5	2.39

Solution II.—Concentration = 0.000018 gramme-equivalent per thousand grammes of solution.

Temperature.	Resistance.	Temperature coefficient per cent.
1°	12418	3.29
5	10927	3.02
10	9433	2.81
15	8272	2.51
20	7327	2.37

Thus the temperature coefficient increases as the dilution gets greater, and also as the temperature falls.

This variation is also shown in some numbers given by KOHLRAUSCH* for the conductivity of potassium chloride solutions of different concentrations. For a normal solution, the conductivity at 0° is 0.06541, and at 18° is 0.09822, the ratio of these numbers being 1.50. For a solution whose concentration is $\frac{1}{100}$ normal, the corresponding figures are 0.000776 and 0.001225, giving a ratio of 1.58.

Thus, in each case, the difference in conductivity between 0° and 18° is greater for the more dilute solution. Now the conductivity of a solution depends on two factors: (1) the amount of ionization, (2) the velocities with which the ions move while active. These velocities are increased by heating the solution, owing to a decrease in what we may term the ionic viscosity, and at extreme dilution, when, in such salts as potassium or barium chloride at any rate, the ionization is practically

* 'Annalen der Physik und Chemie,' N.F. vol. 64, p. 441, 1898.

complete, the temperature coefficient of conductivity is determined by the change in the velocities only. Since the temperature coefficient decreases as the concentration increases, it must follow that, in the case of these salts, the effect of temperature on the ionization is of opposite sign to its effect on velocity, so that heating the solutions decreases their ionization. The curves giving the variation of ionization with concentration at 18° will, therefore, be more steeply inclined to the axis of concentration than the curves for the same quantity at 0° , and, in order to get satisfactory comparisons with freezing point measurements, it is necessary to make conductivity measurements at 0° , and to carry the dilution to such an extent that the limiting value of the equivalent conductivity can be directly estimated. This point will be again considered later, and ionization curves given for 18° as well as for the freezing point.

The measurements of the freezing points of dilute solutions which have been hitherto made show great divergences when the values obtained by different observers are compared, though the results of any one observer often agree well among themselves. The experimental knowledge of this side of the question must be regarded as even more unsatisfactory than that of the electrical conductivity.

In the course of the year 1897, Mr. E. H. GRIFFITHS and the present writer undertook the further experimental investigation of the subject. Mr. GRIFFITHS arranged to make the freezing point determinations by the method of platinum resistance thermometry. The following paper contains an account of the corresponding measurements of the electrical conductivities. Mr. GRIFFITHS proposes to publish a separate account of his experiments when finished, and this will be followed by a joint comparison of the two lines of research.

SECTION 1.—*On the Preparation of the Solutions.*

In investigations of the variation of electrical conductivity with concentration, it has been usual to begin with a solution of the maximum concentration required, and to gradually dilute it till the desired limit was reached. This method involves the use of a very large volume of water, the quality of which must be constant. It also involves the pouring of the solutions into and out of the electrolytic cell at each dilution. Impurities are always liable to enter the liquids during this operation, especially when, as in this investigation, the temperature of the liquids is so low that aqueous vapour from the air must be condensed on their surfaces.

The alternative method of beginning with the pure solvent and gradually adding weighed quantities of a stock solution, seemed, on the whole, better suited to the case. The conductivity of the actual sample of solvent used for the solutions could then be determined for each series of observations, and, since the addition of the successive amounts of stock solution could be made in the electrolytic cell itself, the necessity of pouring the liquids backwards and forwards would be obviated. This not only eliminated errors due to the taking up of impurities, but also effected a

valuable saving of time which would otherwise have been lost in cooling each solution after it had been diluted and returned to the cell.

It had at first been intended to transfer each solution from the freezing point apparatus to that in which the resistance was to be measured, or *vice versa*, so that experiments for the determination of both constants might be made on identical solutions. This could not be done if a series of solutions was made up in either apparatus itself. But the advantage to be obtained is not so great as at first sight appears, since it is unwise to move dilute solutions through air, or to cool them more often than necessary. Moreover, by using water prepared in the same way for each series of experiments, and adding stock solution by similar methods, it seemed that strictly comparable results would be obtained.

SECTION 2.—*On the Electrolytic Cell.*

Having settled, then, that the solutions were to be prepared separately in the two sets of apparatus, it remained to devise a cell to contain the liquids while their resistances were being measured.

It seemed likely that some of the discrepancies between the results of different measurements of freezing points might be due to the action of glass dissolved from the containing vessel. It was therefore decided to carry out the freezing point work in platinum vessels only, and to preserve both the water used and the solutions from all contact with glass. Similar precautions were therefore taken in the resistance measurements.

The following conditions had to be satisfied in the design of the apparatus:—

1. The cell itself and all parts which might by any means touch the liquids contained in it must be of platinum.
2. There must be two insulated platinum electrodes, rigidly fixed relatively to each other. Since the vessel was to be made of a conducting substance, it was evident that its walls must be used as one of the electrodes.
3. Small changes in the level of the liquid must not appreciably affect the electrical constant of the cell.
4. The temperature of the vessel and its contents must be under easy and efficient control.
5. Means of emptying and filling the cell must be provided, and also of adding stock solution to the cell when in position.
6. Stirring apparatus must be arranged to secure uniform temperature, and to mix the stock solution when added with the former contents of the cell.

After many alterations and one complete reconstruction, the apparatus assumed the form shown in section (fig. 1).

The walls (*a*) of the platinum vessel are used as one electrode, a platinum cage (*b*) suspended near its centre, forms the other. This cage, consisting of a short hollow

cylinder, is attached by means of four arms to a platinum tube which passes out through a wide aperture in the top of the vessel, and is rigidly fitted into a longer brass tube (*c*). The brass sheath is kept in place by ebonite rings (shaded in the drawing), and, with all its supports, is therefore insulated from the platinum vessel.

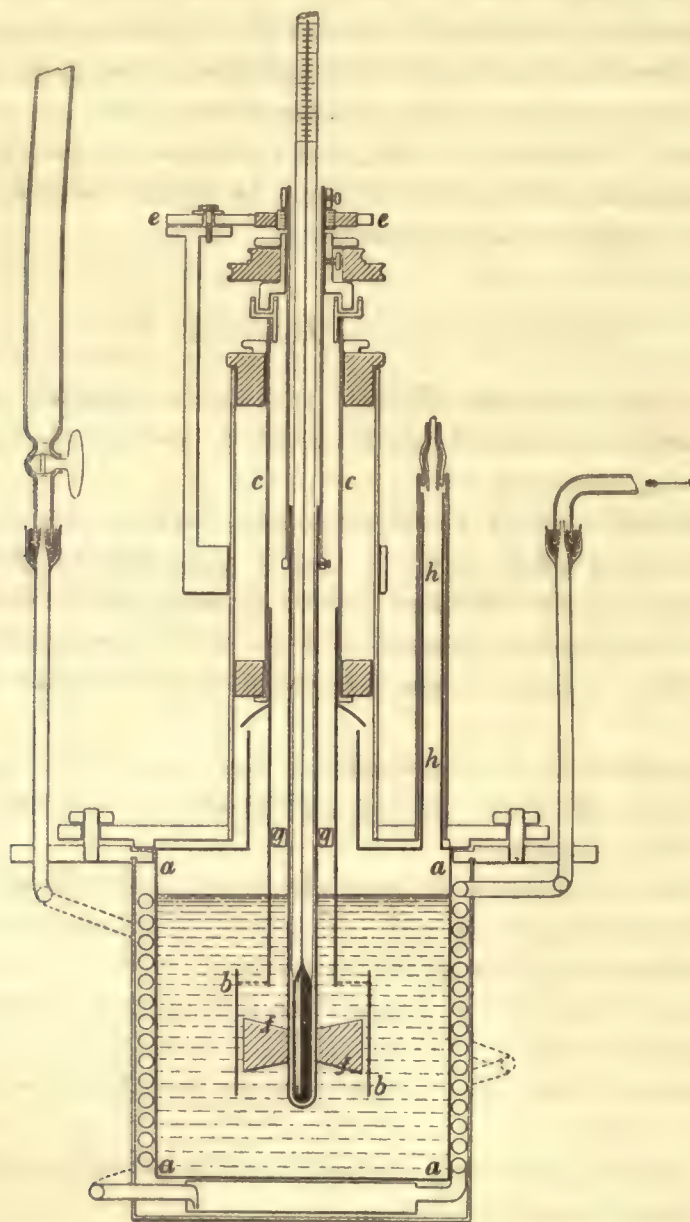


Fig. 1.

A platinum umbrella, attached to the vertical tube, overhangs the opening into the cell, without touching its sides, and thus prevents any dust or other foreign matter from falling into the solution.

Inside the vertical platinum support carrying the cage is fixed a pierced gold

plug (*g*), through which a central platinum tube can freely revolve. The top of this platinum is firmly attached to a brass sheath passing through a steel bearing. The bearing is carried by an ebonite plug, fixed in a horizontal brass arm (*e*), which is supported from the outside of the apparatus by a rigid vertical rod. The whole central system then can revolve round a vertical axis, the steel ring at the top and the gold plug below acting as bearings. The use of this central tube is twofold. In it a mercury thermometer, graduated to $\frac{1}{100}$ th of a centigrade degree, is placed, contact with the platinum walls being secured by the addition of a few drops of mercury. Secondly, it serves as the shaft of a platinum screw (*f*), shaped like a ship's propeller, which, when it revolves, causes a downward current of water through the platinum cage, and thus mixes the whole volume of solution. The shaft bears an ebonite wheel at its top, which is turned when necessary by a hand wheel and cord.

A second opening gives access to the interior of the cell, and a platinum tube (*h*), about 8 millims. in diameter, springs vertically upwards from it. This tube has an outer brass case, which can be closed by a stopper made of a piece of glass rod covered with india-rubber tubing. When the stopper is in its place, no air can enter the cell by this passage, and the only connection between the interior and the atmosphere is at the top of the central screw shaft. How to close this aperture was a problem of some difficulty. If the shaft were allowed to revolve in a simple hole, it would have been apt to grind away fragments, which would have fallen into the liquid below, while if the opening were left free, moist air would enter and water, condensing inside the cold tube, would run down into the platinum vessel. In order to prevent any such effects, the arrangement represented in the figure was adopted. A brass ring with a rim projecting downwards, is fixed to the central shaft, and revolves with it. The rim fits loosely, without touching, into a groove cut in a brass collar which lines the inside of the brass supporting tube. Any air then has to pass over these cold metal surfaces before it can enter the apparatus, and if any moisture is condensed, it is caught in the groove and can be removed.

The platinum vessel and the vertical tubes fixed to its roof, are surrounded with a stout brass case, a thin air-space being left between them. In this air-space the cooling apparatus is disposed. It consists of a shallow rectangular box, placed below the platinum vessel, into which a tube is led through the outer brass case. The tube ends in a nozzle opening near the bottom of the case, and through it a small quantity of ether can be introduced. Dry air is then sucked through; the ether evaporates, and its vapour passes with the current of air along a spiral coil of tubing which closely surrounds the platinum vessel. The evaporation absorbs heat, and the temperature of the whole apparatus slowly falls.

The outer brass case is fixed by means of three projecting arms in a large copper tank of about 30 litres capacity, which can be filled with broken ice. The tank is placed in a large rectangular box of wood and covered by a lid when measurements are being made.

The apparatus is filled from a platinum vessel, which is an exact model on a larger scale of the filling machine used to add stock solution and is shown in fig. 2. The vessel is arranged to hold 250 grammes of water, and about that quantity is collected in it and accurately weighed. The long limb of the vessel being introduced into the cell, a slight increase of pressure is given by removing the platinum stopper and placing a tube of thick india-rubber lightly on its top. At the other end of the india-rubber is a glass tube, part of which is packed tightly with cotton wool. A slight puff of air at the glass tube is then sufficient to start the water siphoning over into the cell. This goes on till the whole quantity of water has entered the cell.



Fig. 2.

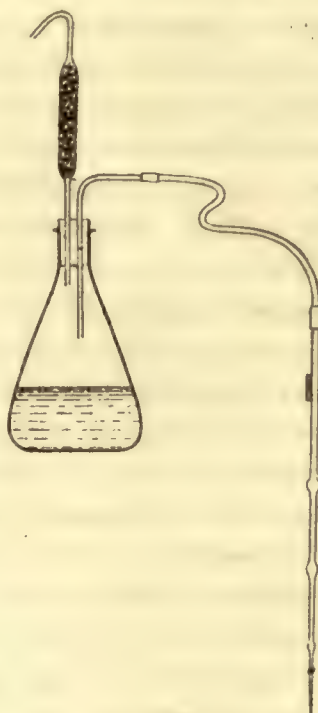


Fig. 3.

The water is then left for some hours till its temperature has sunk nearly to the freezing point. This process can be much accelerated if desirable by the ether apparatus. It is then necessary to adjust the level of the liquid. This is done by means of the glass emptying vessel (shown in fig. 3), through the cork of which pass two tubes. One of them is connected by means of india-rubber with another glass tube, which carries a short piece of very fine platinum tubing at its end. The bore of this is so small that a fine needle will only just enter it. The glass stem will pass into the platinum tube which forms the side entrance to the cell in fig. 1. At its upper end is fixed a glass ring which is too big to enter, and lies on the top of the platinum. When this ring is pressed home, the bottom of the fine platinum tube is in a perfectly definite position inside the cell. In order that it should always withdraw to exactly the same level, it is necessary that the

exhaust pump applied should give a constant (negative) pressure. This is secured by the means shown in fig. 4. The exhaust pump is connected with one arm (*a*) of a T-piece, the other arm (*b*) going to the emptying vessel, and the leg (*c*) passing through the cork of a tall glass bottle. This cork is also pierced by a second tube (*d*) open to the air above, which dips a certain fixed distance below the level of the water in the bottle. When the pump works, a constant stream of bubbles passes through, thus keeping the pressure equal to that of the water column.

By this means liquid is sucked up from the cell into the emptying vessel, and the quantity in the cell when the operation is over, is found to be the same on different occasions to within one or two-tenths of a gramme. Since the whole quantity is more than 200 grammes, this gives an accuracy greater than one in a thousand. (See p. 333.)

Stock solution is added by means of the apparatus shown in fig. 2. A quantity of solution is placed in the platinum vessel and accurately weighed. According to circumstances the quantity varies from .25 to 20 grammes. The long platinum siphon is then inserted into the cell, and a slight pressure applied by placing the india-rubber tube, already described, on the neck of the vessel. The solution then runs over, and the last drops are ejected by another gentle blow. The filling vessel is removed and reweighed, the liquid is mixed by means of the hand wheel and cord, and the apparatus is ready for an observation.

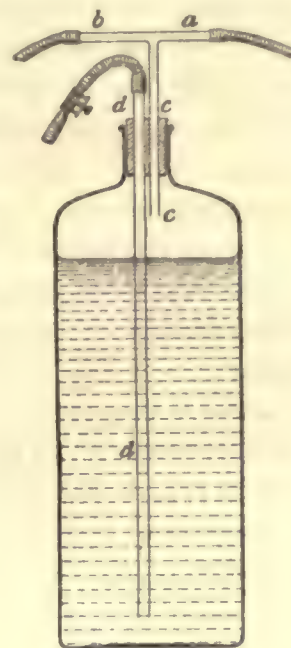


Fig. 4.

SECTION 3.—*On the Surface of the Electrodes.*

It is usual in experiments on the resistance of electrolytes to coat the electrodes with a layer of platinum black, the result of which is to increase the effective area of the plates, and so diminish polarization. In the telephone method, this platinization is necessary, for without it silence cannot be obtained by adjusting the Wheatstone's bridge, except, perhaps, in the case of very highly resisting solutions.

Platinized electrodes, however, are troublesome to use at high dilution. They seem to have the power of extracting the salt from a solution, and of condensing it on their surfaces. Thus, if a dilute solution be placed in a cell with clean platinized electrodes, the resistance will rise for some time—the concentration of the solution seems to get less. If the solution be removed, and pure water, or a solution more dilute than the first, be substituted for it, some of this occluded salt seems to come out, and the resistance of the cell falls.

Now the galvanometer used in this work is much less liable to disturbance by

polarization effects than the telephone indicator, and it was hoped that, considering the large area of the electrodes, platinization might be unnecessary. Measurements were therefore made with the bright platinum surfaces. It was, however, found that, while the results were satisfactory at extreme dilution, the resistances came out higher than they ought as the concentration of the solutions increased.

The cell was therefore platinized by passing a current from two accumulator cells backwards and forwards between the electrodes through a solution of platinum chloride containing a little lead acetate.* It then became very difficult to keep the resistance of a dilute solution constant. It either slowly increased owing to absorption of salt by the electrodes, or slowly diminished as the absorbed salt was given out again to the solution.

Mr. GRIFFITHS suggested that the surface obtained by heating platinum black might answer the purpose required. When heated to redness, a platinized surface becomes of a dull grey colour, and apparently loses its spongy texture. It gives, however, a rough surface, the area of which is much greater than that of a bright polished plate. The cell was dismantled, and the platinum portion heated for some time to bright redness in a large blow-pipe flame.

The surface thus obtained seemed to be quite satisfactory. The absorption effects were apparently done away, and the area of the electrode was large enough to make it possible to measure resistances as low as 10 ohms. Thus, in one apparatus, resistances varying from 10 to 50,000 ohms were easily measurable to an accuracy of one part in a thousand.

SECTION 4.—*On the Measurement of the Electrical Resistance.*

Since very dilute solutions were to be examined in a platinum apparatus, the method of direct currents applied successfully by STROUD and HENDERSON† to the measurement of electrolytic resistances could not be adopted, and alternating currents had to be used. The application of these by KOHLRAUSCH, OSTWALD, and others, a telephone acting as indicator, is too well known to need description, but the method adopted in these experiments, in which the telephone is replaced by a galvanometer, is not so common.

It was first described by FITZPATRICK,‡ and the commutator used by him was lent by the Cavendish Laboratory for the earlier part of the present work. An instrument of improved design was afterwards employed, which is represented in fig. 5. A vulcanite drum, revolving round a horizontal axis, has, near each end of its circumference, a series of brass strips fitted into it, alternate strips at each end

* Lummer and Kurlbaum, 'Ann. der Physik und Chemie,' vol. 60, p. 315, 1897.

† 'Proc. Physical Soc. of London,' vol. 15, p. 13, 1896.

‡ 'Brit. Assoc. Report,' 1886, p. 328.

being in electrical connection with each other, and with one of two brass rings which are fitted in vulcanite beds on to the axis of the drum. A pair of wire brushes are brought into contact with the brass rings, and another pair touch the strips as they revolve. The leads from a single dry cell are connected with the first pair, and the second pair are led to the places on a box of resistance coils at which the battery wires are usually attached in the Wheatstone's bridge arrangement. The drum was at first made to revolve by means of an electric motor; a hand-wheel was afterwards found more convenient. Thus the current from the battery is made to alternate rapidly before it reaches the box of coils.

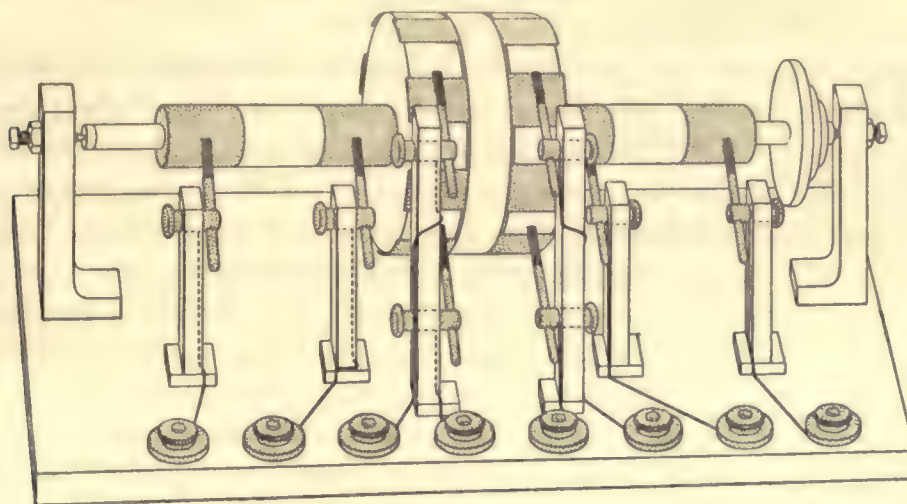


Fig. 5.

The other end of the drum is arranged in an exactly similar manner, except that the brass strips are rather narrower, and the intervening areas of vulcanite rather broader. One pair of brushes is connected with the galvanometer terminals of the Wheatstone's bridge, and the other pair with the terminals of the galvanometer itself. Thus the galvanometer connections are alternated synchronously with those of the battery, the galvanometer being taken out of circuit a little before the battery, and thrown into circuit a little later. By this means the current, which alternates while it is passing through the electrolytic cell, is again made direct before it reaches the galvanometer, the deflection of which can therefore be used as an indication of the direction in which the resistances must be changed in order to get a balance.

The galvanometer used was made on the D'Arsonval principle, and was constructed by Messrs. Nalder Bros. This type has important advantages over the Thomson form. It is quite sensitive enough for the present purpose; its freedom from magnetic disturbances is useful; above all, the large moment of inertia and slow period of swing of the suspended portions prevent small residual periodic disturbances from annoying the observer. This enables very low resistances to be measured.

When thus arranged the method is very satisfactory. All periodic disturbances,

such as those due to self-induction or electrostatic capacity, are eliminated as soon as a certain speed of the drum is attained, and beyond this speed variations in angular velocity throughout a very wide range can be made without appreciably changing the measured resistance. The only effect of such disturbances is to make the galvanometer unsteady when the resistance of the solution falls below a certain value (about 10 ohms in the apparatus used), and to make it rather less sensitive when a very high resistance is measured, such as that of the water used as solvent. This latter effect is chiefly due to the electrostatic capacity of the resistance coils as usually wound, and it has been reduced by the employment of a new set of coils specially wound in sections by Messrs. Elliott Brothers, as described by CHAPERON,* which enables higher resistances to be accurately measured.

As the drum revolves, very considerable thermo-electromotive forces are set up at the contact of the brushes with the commutator, but these do not affect the galvanometer when the drum is in motion, for the currents due to them are reversed so rapidly that they produce no resultant deflection. This can be proved as follows. The galvanometer is disconnected from the circuit, and its position of equilibrium observed. It is then connected up again, and, if the drum has lately been at work, and the resistances in the circuit are low, a considerable deflection, due to the thermal effects, is observed while the drum is at rest. The drum is then revolved, and the galvanometer will be found to return to its normal equilibrium position.

The success of the method of electrical measurement is best shown by the constancy of the observed resistance of a solution when the current through it is changed, or an alteration made in the ratio between the arms of the Wheatstone's bridge. As an example the following numbers are taken from experiments on a barium chloride solution :—

Resistance in battery circuit.	Ratio arms of bridge.	Temperature of solution.	Resistance of solution.
1000	1000 : 100	·15	83·68
1000	1000 : 10	·16	83·69
0	1000 : 10	·20	83·61

SECTION 5.—*On the Temperature to be used.*

The freezing point of a solution gives, as we have seen, a means of calculating the ionization of the solute at that particular temperature. In order that the ionization as calculated from the electrical data should be strictly comparable with this, the ratio of the value of the equivalent conductivity of the given solution to that at

* 'Comptes Rendus,' vol. 108, p. 799, 1899.

infinite dilution should be found for the temperature of the freezing point of the solution. It is simpler, however, to measure all the conductivities at the freezing point of water, and to refer them to the limiting value of the equivalent conductivity at that temperature. The freezing point of the strongest solution used is less than a tenth of a degree below zero, and, since the temperature coefficient of conductivity only changes very slowly as the concentration of the solution alters, the maximum error introduced by this simplification will be less than the unavoidable errors of experiment.

SECTION 6.—*On the Testing of the Apparatus.*

Insulation of the Electrodes.—While the cell was empty it was connected up in series with a dry battery and the galvanometer. This was repeated at intervals throughout the work. Sometimes no deflection could be seen, sometimes the movement was just visible. In either case, the leakage between the electrodes was negligible for the purposes of the experiments.

Adjustment of the Liquid in the Cell to a Constant Volume.—The cell was taken to pieces, dried by a current of hot air, and put together again. About 230 to 250 grammes of water were run in from the large platinum filling machine, which was weighed before and after the operation. The water was then cooled to within half a degree of the freezing point, and the emptying machine weighed and placed in position. The exhaust apparatus was next worked at a constant pressure of about a foot of water, till no more water came out of the cell. The increase in weight gave the water withdrawn, and this, subtracted from the weight put in, gave the final weight of water in the cell.

In order to test the constancy of this weight (*i.e.*, the accuracy of the levelling), a weighed quantity of water was introduced by means of the small filling machine, and again withdrawn into the emptying vessel. If all is well, the weight withdrawn should equal that added, and the weight of water left in the cell should keep the same when this process is repeated.

The volume of the cell has to be redetermined whenever it is taken to pieces for cleaning or any other purpose. Details of one such determination are given below. The importance of keeping the withdrawing pressure small and constant is well shown by this example. In the third experiment, by an accident, the full force of the water pump was used, and a variation of nearly half a gramme in the weight of water left in the cell was the result. When more water was added, and a new withdrawal made with the regulator, it will be seen that the right level was again obtained.

August 7, 1899. Volume of Cell.

Weight of water run into cell from the large filling machine.	236·16
Weight withdrawn at 0°·4	16·56
Weight of water in cell.	219·60
Weight added from small filling machine	8·14
Weight withdrawn at 0°·5	8·11
Weight of water in cell.	219·63
[Weight added	9·27
Weight withdrawn at 0°·5	8·85
(Full pressure of water pump)	
Weight of water in cell.	220·05]
Weight added	9·47
Weight withdrawn at 0°·6	9·93
Weight of water in cell.	219·59
Mean value	219·61

Another example, August 20, 1899.

Weight of water in cell : 219·25, 219·36, and 219·34. Mean = 219·32

Thus the greatest error introduced into the value for the concentration of the solutions by this part of the operations is about one in two thousand.

Constancy of Resistance of the Solvent.—During the early stages of the work it was found impossible to keep the resistance of the water in the cell at a constant value for any length of time, rapid increase in conductivity always appearing. This change occasioned great difficulties, in fact months were given to the investigation of its cause and cure. It seemed to be due to the gradual absorption of traces of impurity (such as carbonic acid, &c.) from the atmosphere, for whenever a fresh quantity of air found its way into the apparatus, the resistance fell for some time, the fall being quicker when the screw was kept in continual motion. It was therefore found advisable to fill the cell for some time before using it, for while the contents were cooling, air was of course being drawn in, and, until all the impurities in that volume of air had been absorbed, no constancy of resistance could be obtained. Again, when the contents were levelled, water was drawn out, and, therefore, air entered to replace it, and this also caused variation for some little time. This leakage of air also occurred when salt had been added, chiefly at the moments when stock solution was being introduced into the cell. Its effect was to change the form of the ionization curves for dilute solutions, the impurities as they gradually accumulated

causing a rise in the apparent equivalent conductivity till the quantity of salt added was so great that the error became unimportant.

The apparatus was eventually moved to a room in which no gas flames were allowed, and the cell more carefully shielded from the atmosphere. Much greater constancy in the resistance of the solvent was thus obtained, though even after the removal a slight deterioration in quality sometimes appeared. As an example of a rather bad case the following numbers may be given. They show the resistance of the water used as solvent for a series of solutions of potassium chloride.

December 16, 1898. KCl at 0°. Resistance of water.

Time.	Temperature.	Resistance.
10 ^h 0 ^m	-0.10	34400
10 12	-0.02	34260
10 26	+0.01	34140
11 26	+0.11	33890
11 29	+0.12	33850
11 42	+0.13	33810
11 46	+0.13	33790

The resistance of the first solution was measured at 11.50, at which time the slight falling off still noticeable in the water would have brought its resistance to about 33770 at +0.13. The freezing point of water on the thermometer as used was +0.08, and this resistance corresponds to 33818 at that temperature. The reciprocal of this number, viz., 2.957×10^{-5} , may be taken as a measure (in arbitrary cell units) of the conductivity of the solvent; it has to be subtracted from the corresponding value for the solutions.

The constancy was usually greater than this, and it was found that water could be added from the filling machine without changing the measured resistance, except by the small amount due to the increase in volume of the liquid and the slight rise in temperature caused by the addition of warmer water. This is shown by the following figures :—

July 30. Resistance of Water.

Time.	Temperature.	Resistance.
12.32	.09	34420
12.35	.06	34340
12.39	.05	34310
12.44	.05	34260
12.47	.06	34190

·35 gramme of water was then added from the filling machine.

12.50	·12	34010
12.55	·13	33920
1.10	·18	33750

Considering that the resistance of the solvent only comes in as a correction of the observed resistances of the solutions, the slight change, if any, which these figures show is quite negligible.

SECTION 7.—*On the Preparation of the Water.*

Great difficulties occurred in getting water of quality good enough for the experiments. The process finally adopted was as follows: Tap water was boiled to precipitate calcium carbonate, and filtered through paper. It was mixed with potash and potassium permanganate till the colour became a deep purple, and then distilled from a copper still. The water (No. 1) so obtained was redistilled from a big Jena glass flask with a much smaller quantity of alkaline permanganate. The product (No. 2) of this operation was placed in a large platinum still, a very small quantity of acid potassium sulphate was added, and the water (No. 3) was slowly collected in platinum vessels. The platinum still stood on a screen of sheet copper in order to shield it from the products of combustion of the gas burner. In all the distillations the first and last portions of water obtained were rejected, together about one-third of the whole. The water thus prepared, when measured in the platinum cell at 18°, had an average conductivity of about 9×10^{-15} C.G.S. unit. The best water obtained by KOHLRAUSCH* by distillation in air had a conductivity at the same temperature of 7×10^{-15} , while by distilling *in vacuo* a value as low as 2×10^{-15} was reached.†

SECTION 8.—*On the Preparation of the Stock Solutions.*

Miss D. MARSHALL was good enough to prepare some of the stock solutions for the early part of the work, and Mr. H. J. H. FENTON kindly allowed most of those used in the later experiments to be made up under his advice by Mr. GEORGE HALL, at the Cambridge University Chemical Laboratory. Details of the methods are given in Section 11, under the heading of each substance. The concentration of these solutions was in general about one-third to one-half normal. They were made up and kept in Jena glass flasks accurately stoppered. Glass is less soluble in salt and acid solutions than in pure water, and, under any circumstances, the small quantities

* Kohlrausch und Holborn, 'Leitvermögen der Electrolyte,' p. 411.

† Kohlrausch und Heydweiller, 'Wied. Ann.,' vol. 53, p. 209, 1894.

of these strong solutions ultimately used, make the use of glass harmless for the purpose of storing them.

A second stock solution (*b*) was then prepared from one of these (*a*) solutions. About 2 grammes of (*a*) were weighed out in the small filling machine, and run into a platinum bottle. Water of the same quality as that to be used as solvent in the platinum cell was then added till a dilution of about one in forty was reached. This gave to solution (*b*) a concentration of about one-hundredth normal, and enabled a solution of about one hundred-thousandth normal to be obtained in the cell by the addition of about .25 of a gramme of stock solution.

The atomic weights used in calculating the equivalent concentrations were the same as those taken by KOHLRAUSCH for his latest results. The following list shows their values :—

Hydrogen	1.008	Potassium	39.14
Carbon	12.00	Chromium	52.14
Nitrogen	14.04	Manganese	55.0
Oxygen	16.00	Iron	56.02
Sulphur	32.06	Copper	63.6
Chlorine	35.45	Barium	137.4

SECTION 9.—*On the Method of Experimenting.*

The method of conducting a series of measurements was as follows :—

The cell was thoroughly washed, water being put in and sucked out with an air-pump several times. The copper tank was then filled with broken ice, and about 250 grammes of water of the best quality were run into the cell, which was then left for several hours till the temperature of the contents had sunk nearly to zero. It was found advisable to fill the cell the evening before an experiment was made, and leave the water in it for the night. The level of the water was adjusted with the emptying apparatus, and its temperature lowered, if necessary, by evaporating ether through the spiral coils, till it stood within one-tenth of a degree of zero. The resistance was then measured at intervals of five minutes, the screw being worked between each observation.

The conductivity of the solvent having reached a practically constant value, a small quantity (usually about .25 of a gramme) of stock solution (*b*) was placed in the filling machine, and run into the cell. As soon as it had entered, the screw was turned till mixture was complete. This, it was found, was usually the case after about six revolutions of the hand wheel, but more were generally given. A resistance measurement was then made and repeated at intervals while the weighings necessary for the next experiment were being performed. The value of the resistance should be practically constant throughout.

A second quantity of stock solution (*b*) was then added and the process repeated,

the amounts being gradually increased, till the whole quantity of stock solution (b) in the cell was about 10 grammes. The liquid had then to be levelled. It was at first intended to add larger quantities of a weaker stock solution and to level the liquid for each observation, but it soon became evident that the errors would be much reduced in all directions if this mode of procedure was abandoned, and a correction for level applied to the measured resistance. This correction was determined by experiment, and, in the final state of the cell, was found to be '31 per cent. for each gramme of liquid in the cell above the normal amount.

By this means it was only necessary to level when the total quantity added amounted to about 10 grammes, and the consequent change of level in the liquid in the cell was about one quarter of a centimetre. Thus one or two levellings were usually enough for a complete set of observations on any one substance.

When the quantity of solution (b) added to the liquid in the cell reached about 10 grammes, it became possible to use solution (a), for the equivalent quantity of that solution was about '25 gramme, an amount which could be weighed with care to the necessary accuracy of one part in a thousand. By the time that about 10 grammes of (a) had been added, the resistance had usually sunk to the value at which accurate measurement became impossible, and the experiments were stopped.

At intervals throughout the experiments it was necessary to adjust the temperature by means of the ether apparatus. It was generally possible to keep the solutions within the limits of a tenth of a degree above or below zero. While small quantities of solution were being added it was not necessary to cool between each experiment, but when a gramme or more of liquid at the temperature of the room was run in, the liquid in the cell was heated through several tenths of a degree, and had always to be cooled by the ether apparatus. These opportunities were taken to determine temperature coefficients for the small corrections necessary on the observed values of the resistances.

SECTION 10.—*On the Reduction of the Observations.*

1. *Calculation of the Concentration.*—The weight of the stock solution (b) added for the first experiment is multiplied by its concentration in terms of gramme-equivalents of solute per gramme of solution. This gives the number of gramme-equivalents of solute present in the cell. The weight of solution in the cell is equal to the weight of water left after levelling (which is known from separate and preliminary experiments) plus the weight of stock solution added, and the weight of solvent is equal to the weight of solution minus the weight of solute added. Thus the concentration of the solution can be calculated in terms of gramme-equivalents of solute per thousand grammes of solution or per thousand grammes of solvent. These values are sensibly the same while the solutions are dilute, and the difference only becomes appreciable for the two or three strongest solutions of each set. Throughout this

paper the strengths are referred to 1000 grammes of solution. Let us denote this concentration by the symbol m . When a second quantity of solution is put into the cell, we have to add the amount of solute in it to the amount already present in the cell in order to calculate m .

It will be noticed that, as long as we simply add successive quantities of stock solution without withdrawal, the values of m , calculated in terms of weights, are independent of any contraction on mixing the liquids. If this contraction is appreciable, we shall find that, when we come to level the solution, the weight withdrawn is a little less than the total weight of stock solution added. From a knowledge of the weight withdrawn, however, we can deduce the weight left in the cell, and this is the weight we must use in subsequent calculations. The results will then be independent of any contraction which may have occurred.

From the value of the concentration in terms of the weight of solvent, we can calculate the number of solvent molecules which are present to each molecule of solute. The molecular weight of water being 18, the number required is the reciprocal of $m \times \frac{18}{1000}$ or $\frac{1000}{18m}$ for those substances like potassium chloride in which the molecular is also the electrically equivalent weight, and for bodies such as sulphuric acid, whose equivalents are $\frac{1}{2}\text{H}_2\text{SO}_4$, &c., its value is $2 \times \frac{1000}{18m}$. These values are tabulated as N in the final results.

2. *Calculation of the Conductivity.*—The mean value of the resistance of a given solution in the cell and the mean temperature at which the measurements were made are calculated from the observations. The temperature is usually within a tenth of a degree of zero, so that an approximate knowledge of the temperature coefficient is enough to enable the resistance at the freezing point to be deduced with sufficient accuracy.

This value has then to be corrected for the level. The liquid in the cell stands higher than it did at the beginning, or after the last withdrawal, by an amount proportional to the total weight of solution which has subsequently been added. It is known that 1 gramme withdrawn from the liquid increases the measured resistance by .31 per cent., so that it is easy to calculate what the resistance would be in each case if the solution were levelled by means of the withdrawing apparatus.

The value thus found is entered as R in the tables of results. Its reciprocal is a measure, in arbitrary units, of the conductivity of the solution, and, if the corresponding value for the conductivity of the solvent is subtracted from it, we have a measure of the conductivity of the solute at a given dilution, on the assumption that the conductivity of a mixture is equal to the sum of the conductivities of its constituents. This supposition is always correct for salts like potassium chloride, &c., in which conductivity is proportional to concentration at great dilution, for in stronger solutions the correction for the solvent becomes inappreciable. For solutions of acids,

we shall find that at extreme dilution the equivalent conductivity decreases rapidly as concentration is reduced, and in such cases perhaps the best way for the present would be to make no correction for the solvent, but to wait until more about its action is understood. But the equivalent conductivities of acids are much greater than those of salts, owing to the high velocity of the hydrogen ion, and in them the correction for the solvent is therefore smaller. And so to preserve uniformity, the correction is made in the measurements on sulphuric acid which follow. Its effect will not appreciably change the general direction of the curve giving the results.

Having thus determined the value of the concentration m and of the conductivity k of the substance dissolved, we get k/m , the equivalent conductivity.

In order to express the results in a visible form, we may plot a curve with the values of k/m as ordinates, and the values of $\sqrt[3]{m}$ (a number proportional to the average nearness of the molecules of solute) as abscissæ. This gives a curve in which the very dilute portion is not crowded together as it would be if we took the values of m itself as abscissæ, and, moreover, the fact that most of the curves so drawn come out as straight lines for the greater part of their length seems to indicate that there are theoretical as well as practical reasons for choosing this method. The form of these curves is similar to that of the corresponding ionization curves shown in the diagrams. It will be seen that as the concentration of a solution gets smaller, the value of k/m approaches a limiting value. Its maximum can easily be determined from the curve in such cases as potassium chloride or barium chloride, where the slope of the curve is comparatively small and the limit is reached at moderate dilutions. In cases such as those of potassium bichromate and potassium ferricyanide, the maximum values are more uncertain, and this uncertainty is transferred to the ionization curves deduced from them.

The maximum value having been estimated, the coefficient of ionization, α , is calculated for each solution by dividing the equivalent conductivity by its maximum value, and the curves given below show the results obtained by plotting the ionizations as ordinates and the values of $m^{\frac{1}{3}}$ as abscissæ.

It will be noticed that, in order to get these ionization coefficients for a solution of any given concentration, it is not necessary to know the absolute value of the equivalent conductivity. For the purposes of these experiments, then, there was no need to measure the constant of the electrolytic cell. To do so satisfactorily would have involved a redetermination each time the cell was dismantled. The approximate values of the equivalent conductivities have, nevertheless, been calculated for convenience of reference; but it must be understood that their accuracy is not supposed to be as great as that of the ionizations, which are quite independent of their absolute values.

SECTION 11.—*On the Results of the Measurements.*

Sulphuric Acid.—As an example of the method of work, and of the way in which

the observations were recorded, full details from the laboratory note-book are given on p. 342, for a set of measurements on sulphuric acid. This set is chosen as a fair example of the usual degree of constancy among the measurements of resistance. It is also shorter than any of the others, owing to the fact that sulphuric acid had been investigated in the preliminary experiments, and could thus be disposed of in a fewer number of observations. Four other solutions, stronger than any of this set, were afterwards made up, and their resistances determined in a Jena glass cell. The results of these are included in the final table on p. 343.

Sulphuric Acid (prepared at the Chemical Laboratory).—A quantity of redistilled sulphuric acid was taken, and the percentage of H_2SO_4 found. Then a known weight of SO_3 was obtained, and the calculated quantity of the sulphuric acid was added to bring it up to 100 per cent. H_2SO_4 . The acid was then cooled till crystals separated, and the remaining liquid was drained away. This operation was repeated four times, and finally gave crystals melting at $+10\cdot5^\circ \text{C}$.

Four estimations of the concentration of the solution prepared were made with the following results :—

Weight of solution.	Weight of BaSO_4 obtained.	Grammes of H_2SO_4 per gramme of solution.
38·771	1·6115	·01745
35·4775	1·4780	·01749
39·5265	1·6610	·01764
89·2962	3·7240	·01751

This gives ·01752 for a mean value; solution (a) had therefore a strength of $3\cdot573 \times 10^{-4}$ gramme-equivalent per gramme of solution. For the dilute solution (b) 7·9880 grammes of (a) were diluted to a total weight of 155·80 grammes, giving a strength of $1\cdot832 \times 10^{-5}$ gramme-equivalent per gramme of solution.

Sulphuric Acid. August 3, 1899.

Solution.	Time.	Temperature.		Resistance.		Temperature coefficient.	Weight of filling machine.	Weight of stock solution added.	Total weight of stock solution in cell.	Weight of emptying vessel.	Level.	Volume.
		Obtained.	Mean.	Obtained.	Mean (reduced).							
I.	August 3. 4. 45	.22		41350			—	—	—	—	—	219.42
	4. 55	.23	.26	41000	40420		—	—	—	—	—	
	5. 09	.30		40700			—	—	—	—	—	
	5. 17	.30		40410			—	—	—	—	—	
	5. 24	.32		3060			37.4987	(b) .3902	.3902	—	.39	219.81
II.	5. 41	.39	.37	3070	3106		37.1085			—		
	5. 45	.35		3075			37.8863			—		
	5. 50	.38		3075			37.1276		1.1589	—	1.16	220.58
	5. 53	.41	.42	939.9	954.3		37.8863	.7687		—		
	5. 57	.43		939.9			37.1276			—		
III.	6. 07	.41		940.8						—		
	6. 12	.51	.51	435.7			38.3964	1.2640	2.4229	—	2.42	221.84
	6. 14	.51		435.7	444.7	.028	37.1324			—		
	6. 35	—	.00	441.6						—		
	6. 37	.00		441.7			39.0432	1.9208	4.3437	—	4.34	223.76
IV.	6. 45	.19	.20	243.8	247.8		37.1224			93.33 85.34 7.99		
	6. 47	.21		243.7								
V.	7. 27	.02	—	139.5			40.6288	3.5207	7.8634		—	219.29
	7. 30	.01	—	139.5	139.0		37.1081	(a) .4870	(a) .8760		—	219.78
VI.	7. 35	.02	.06	63.08	63.11		37.5940			—	.36	
	7. 42	.10		63.03			37.1070			—		
VII.	7. 50	.16	.16	37.75			37.7139	.6105	1.4865	—	.97	220.39
	7. 53	.16		37.75			37.1084			—		
	August 4. 9. 45	.80	.77	37.26	37.95					—		
	9. 50	.75		37.41						—		
	10. 20	.01	.00	37.98		.022				—		
VIII.	10. 23	.00		37.98						—		
	10. 30	.08	.10	27.10	27.25		37.7274	.6304	2.1169	—	1.60	221.02
	10. 40	.12		27.08			37.0970			—		
IX.	10. 45	.20	.21	19.90	20.05		37.9207	.8183	2.9852	—	2.42	221.84
	10. 47	.20		19.88			37.1024			—		
	10. 52	.23		19.87						—		

TABLE I.*—Sulphuric Acid. $\frac{1}{2}\text{H}_2\text{SO}_4 = 49.04$.August 3-4, 1899. Solvent, $W = 219.42$. $R = 40420$.

No.	m .	$m^{\frac{1}{2}}$.	R .	k/m .	α .
I.	3.254×10^{-5}	.0319	3106	9.13	.808
II.	9.628 "	.0459	954.3	10.63	.940
III.	2.001×10^{-4}	.0585	444.7	11.11	.983
IV.	3.558 "	.0709	247.8	11.27	.997
V.	6.340 "	.0859	139.0	11.31	1.000
VI.	1.425×10^{-3}	.1125	63.11	11.10	.982
VII.	2.411 "	.1341	37.95	10.92	.966
VIII.	3.423 "	.1507	27.25	10.74	.948
IX.	4.729 "	.1678	20.05	10.54	.932

In Glass Cell. August 6, 1899.

I.	3.660×10^{-3}	.1541	1789	.1528	.946
II.	5.381 "	.1752	1246	.1491	.924
III.	1.158×10^{-2}	.2262	615.7	.1402	.869
IV.	1.769 "	.2596	424.4	.1347	.834

Potassium Chloride.—Recrystallised salt was dried in a combustion tube in a current of dry air.

.3409 gramme was then weighed out and dissolved, the weight of solution (a) being 46.43 grammes.

Solution (a) thus has a concentration of 9.844×10^{-5} gramme-equivalent per gramme of solution.

This was diluted for the second solution (b), the concentration of which was 5.503×10^{-6} gramme-equivalent per gramme of solution.

* After the publication of the abstract of this paper in the 'Proceedings of the Royal Society,' an arithmetical error was discovered in the reduction of the observations on sulphuric acid. The ionizations given here differ slightly, owing to this cause, from those given in the abstract, the difference, however, never exceeding three parts in a thousand.

TABLE II.—Potassium Chloride. $KCl = 74.59$.December 16, 1898. Solvent, $W = 234.05$. $R = 33770$.

No.	m .	$m^{\frac{1}{2}}$.	R.	k/m .	α .
I.	6.236×10^{-6}	.0184	18908	3.740	.999
II.	9.576 "	.0213	15297	3.739	.999
III.	1.801×10^{-5}	.0262	10302	3.736	.998
IV.	3.327 "	.0329	6480	3.742	1.000
V.	5.723 "	.0386	4096	3.745	1.001
VI.	1.170×10^{-4}	.0490	2142	3.736	.998
VII.	1.854 "	.0570	1387	3.728	.996
VIII.	2.926 "	.0663	891.6	3.732	.997
IX.	5.607 "	.0824	472.5	3.722	.995
X.	1.045×10^{-3}	.1014	256.3	3.707	.991
XI.	1.906 "	.1240	141.3	3.696	.988
XII.	3.956 "	.1582	68.87	3.662	.979
XIII.	8.602 "	.2049	32.11	3.617	.966

I.	4.107×10^{-3}	.1600	64.35	3.775	.979
II.	1.138×10^{-2}	.2249	23.77	3.695	.958
III.	2.118 "	.2767	12.98	3.635	.942
IV.	3.699 "	.3332	7.58	3.567	.925

Barium Chloride (prepared at the Chemical Laboratory).—Recrystallised barium chloride was dissolved in good distilled water (No. 1), and recrystallised again in a platinum dish. The remaining liquid was poured off from the crystals, which were redissolved in No. 1 water. The strong solution was cooled, and the new crystals transferred to a funnel and washed with water.

14.358 grammes of $BaCl_2 \cdot 2H_2O$ were then dissolved in 436.45 grammes of No. 2 water. 1 gramme of this solution (a) thus contains .03185 gramme of $BaCl_2 \cdot 2H_2O$.

Two samples of this solution were estimated as barium sulphate by gravimetric analysis, and gave .03178 and .03177 gramme per gramme respectively, the mean value being .031775. The dilute solution (b) used for the observations of Series 6 had a strength of 6.295×10^{-6} gramme-equivalent per gramme of solution. This was prepared by diluting a small quantity of solution (a), the strength of which, calculated in the same terms, gives 2.602×10^{-4} gramme-equivalent per gramme of solution.

TABLE III.—Barium Chloride. $\frac{1}{2}\text{BaCl}_2 = 104.1$.
 July 31, 1899. Solvent, $W = 219.42$. $R = 41160$.

No.	m .	$m^{\frac{1}{2}}$.	R.	k/m .	α .
I.	1.041×10^{-5}	.0219	17070	3.294	1.000
II.	2.418 "	.0289	9615	3.296	1.000
III.	5.245 "	.0375	5069	3.298	1.000
IV.	1.185×10^{-4}	.0492	2422	3.279	.995
V.	2.395 "	.0621	1242	3.261	.989
VI.	5.031 "	.0795	606.6	3.229	.980
VII.	9.636 "	.0988	321.6	3.203	.972

July 30 and 31. Solvent, $W = 219.42$. $R = 33370$.

I.	3.335×10^{-4}	.0693	897.4	3.252	.987
II.	6.358 "	.0860	481.5	3.220	.977
III.	1.145×10^{-3}	.1046	271.3	3.193	.969
IV.	1.826 "	.1222	172.9	3.152	.956
V.	2.774 "	.1405	115.2	3.119	.946
VI.	3.872 "	.1570	83.51	3.085	.936
VII.	5.522 "	.1767	59.50	3.039	.922
VIII.	7.817 "	.1985	42.62	2.999	.910
IX.	1.165×10^{-2}	.2267	29.21	2.937	.891
X.	1.751 "	.2599	19.87	2.874	.872

Copper Sulphate.—Recrystallised salt $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, supplied by KAHLBAUM, of Berlin, as free from iron, was used.

6.6440 grammes of salt dissolved in 130.67 grammes of solution gave a concentration of 4.072×10^{-4} gramme-equivalent per gramme of solution.

From this, solution (b) was prepared, with a concentration of 5.947 gramme-equivalent per gramme of solution.

The same solutions (a) and (b) were used four days later for the experiments at 18° . Solution (b) was weighed after and before use in order to estimate any loss of weight by evaporation or from other causes. The loss observed, .01 in 37.38 grammes of solution, was negligible.

TABLE IV.—Copper Sulphate, $\frac{1}{2}\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 124.87$.
 At 0° . January 15, 1900. Solvent, $W = 219.44$. $R = 33932$.

No.	m .	$m^{\frac{1}{2}}$.	R.	k/m .	α .
I.	9.551×10^{-6}	.0212	17131	3.026	.998
II.	1.822×10^{-5}	.0263	11852	3.013	.994
III.	3.993 "	.0342	6729	2.984	.984
IV.	8.456 "	.0439	3595.2	2.941	.970
V.	1.744×10^{-4}	.0559	1877.2	2.885	.952
VI.	3.878 "	.0730	898.5	2.794	.921
VII.	9.728 "	.0991	388.29	2.617	.863
VIII.	2.542×10^{-3}	.1365	164.03	2.387	.787
IX.	6.632 "	.1879	72.54	2.074	.684
X.	1.473 "	.2451	37.92	1.788	.590
XI.	2.776 "	.3028	22.95	1.568	.517

In glass. Series 2. Solvent, $W = 120.51$. $R = 1370000$. At 0° .

June 30, 1899.

No.	m .	$m^{\frac{1}{2}}$.	R.	k/m .	α .
I.	2.678×10^{-3}	.1389	10890	3.402×10^{-2}	.781
II.	5.607 "	.1777	5781	3.073 "	.701
III.	8.817 "	.2065	3967	2.851 "	.652
IV.	1.281×10^{-2}	.2340	2929	2.659 "	.609
V.	1.753 "	.2598	2277	2.501 "	.572
VI.	2.557 "	.2946	1689	2.313 "	.530
VII.	3.562 "	.3290	1300	2.158 "	.494

TABLE V.—Copper Sulphate—(continued).

At 18° . January 19, 1900. Solvent, $W = 219.25$. $R = 22084$.

No.	m .	$m^{\frac{1}{2}}$.	R.	k/m .	α .
I.	9.068×10^{-6}	.0209	11062	4.976	.999
II.	1.683×10^{-5}	.0256	7776.8	4.948	.993
III.	3.789 "	.0336	4327.7	4.902	.984
IV.	8.654 "	.0442	2160.6	4.825	.968
V.	1.832×10^{-4}	.0568	1096.6	4.731	.949
VI.	3.920 "	.0732	541.72	4.593	.922
VII.	8.921 "	.0963	255.29	4.340	.871
VIII.	1.909×10^{-3}	.1241	129.57	4.018	.806
IX.	3.904 "	.1575	69.68	3.664	.735
X.	8.176 "	.2015	37.78	3.232	.649
XI.	1.460×10^{-2}	.2444	23.81	2.873	.577
XII.	2.452 "	.2905	15.87	2.568	.515

Potassium Permanganate.—Recrystallised salt, supplied from the Chemical Laboratory, was dissolved; 5.3370 grammes in 198.42 grammes of solution.

Solution (a) had, therefore, a concentration of 1.746×10^{-4} gramme-equivalent per gramme of solution.

Two other solutions were prepared from this, having respectively concentrations of 4.255×10^{-5} and 5.014×10^{-6} gramme-equivalent per gramme of solution.

TABLE VI.—Potassium Permanganate, $\text{KMnO}_4 = 158.1$.August 14, 1899. Solvent, $W = 219.61$. $R = 42900$.

No.	m .	m^d .	R.	k/m .	α .	α (corrected).
I.	8.803×10^{-6}	.0207	19660	3.130	.961	1.000
II.	1.750×10^{-5}	.0260	12600	3.200	.982	1.002
III.	3.545 "	.0329	7259	3.227	.991	1.000
IV.	7.120 "	.0415	3926	3.249	.997	1.002
V.	1.422×10^{-4}	.0521	2057	3.254	.999	1.001
VI.	3.279 "	.0689	918.0	3.251	.998	.999
VII.	7.851 "	.0922	389.6	3.243	.994	.996
VIII.	1.687×10^{-3}	.1190	133.3	3.220	.988	.989
IX.	3.051 "	.1451	102.5	3.191	.981	.981
X.	5.002 "	.1710	63.20	3.160	.970	.970
XI.	7.604 "	.1966	41.89	3.135	.962	.962
XII.	1.062×10^{-2}	.2198	30.28	3.106	.953	.953
XIII.	1.411 "	.2417	22.98	3.082	.946	.946
XIV.	1.883 "	.2660	17.40	3.050	.936	.936

Potassium Ferricyanide (prepared at the Chemical Laboratory).—Selected crystals were washed three times with No. 2 water, and a concentrated solution made at 100° , using a water bath. This solution was filtered, and allowed to crystallise, the remaining liquid was poured off, and the crystals again washed, recrystallised as before, washed and drained, heated in a steam oven, and finally dried in a vacuum desiccator for six days. The operations were carried on in a dark room, and Jena flasks were used.

The following solution was made up by gas light. 4.8625 grammes of K_3FeCy_6 were dissolved in 216.52 grammes of No. 2 water, giving a solution of strength 2.002×10^{-4} gramme-equivalent per gramme of solution. From this a second solution was prepared, using No. 3 water; its strength was calculated to be 5.089×10^{-6} gramme-equivalent per gramme.

TABLE VII.—Potassium Ferricyanide, $\frac{1}{3}\text{K}_3\text{Fe}(\text{CN})_6 = 109.9$.August 21, 1899. Solvent, $W = 219.32$. $R = 34060$.

No.	m .	m^d .	R.	k/m .	α .
I.	7.513×10^{-6}	.0196	16580	4.119	.994
II.	1.518×10^{-5}	.0248	10850	4.139	.998
III.	3.339 "	.0322	5990	4.119	.994
IV.	6.642 "	.0415	3313	4.102	.990
V.	1.402×10^{-4}	.0520	1667	4.068	.981
VI.	2.777 "	.0653	870.8	4.030	.972
VII.	7.072 "	.0891	354.3	3.949	.953
VIII.	1.559×10^{-3}	.1159	165.8	3.858	.931
IX.	3.051 "	.1450	87.61	3.732	.900
X.	4.868 "	.1694	56.54	3.633	.877
XI.	7.931 "	.1994	35.81	3.518	.849

Potassium Bichromate (prepared at the Chemical Laboratory).—A recrystallised sample was taken and crystallised twice in a platinum basin, drained, washed, and dried in a water oven, and finally in a vacuum desiccator for seventy-two hours. The operations were carried on as much as possible in the dark.

5.259 grammes of $K_2Cr_2O_7$ were dissolved in 228.130 grammes of water in a counterpoised flask. This gave a solution of 1.529×10^{-4} gramme-equivalent per gramme of solution. For the experiments of Series 2 a dilute solution was further prepared, containing 4.775×10^{-6} gramme-equivalent, and for Series 4 another of strength 3.112×10^{-6} gramme-equivalent per gramme of solution.

TABLE VIII.—Potassium Bichromate, $\frac{1}{2}K_2Cr_2O_7 = 147.3$.

August 16, 1899. Solvent, $W = 219.61$. $R = 33860$.

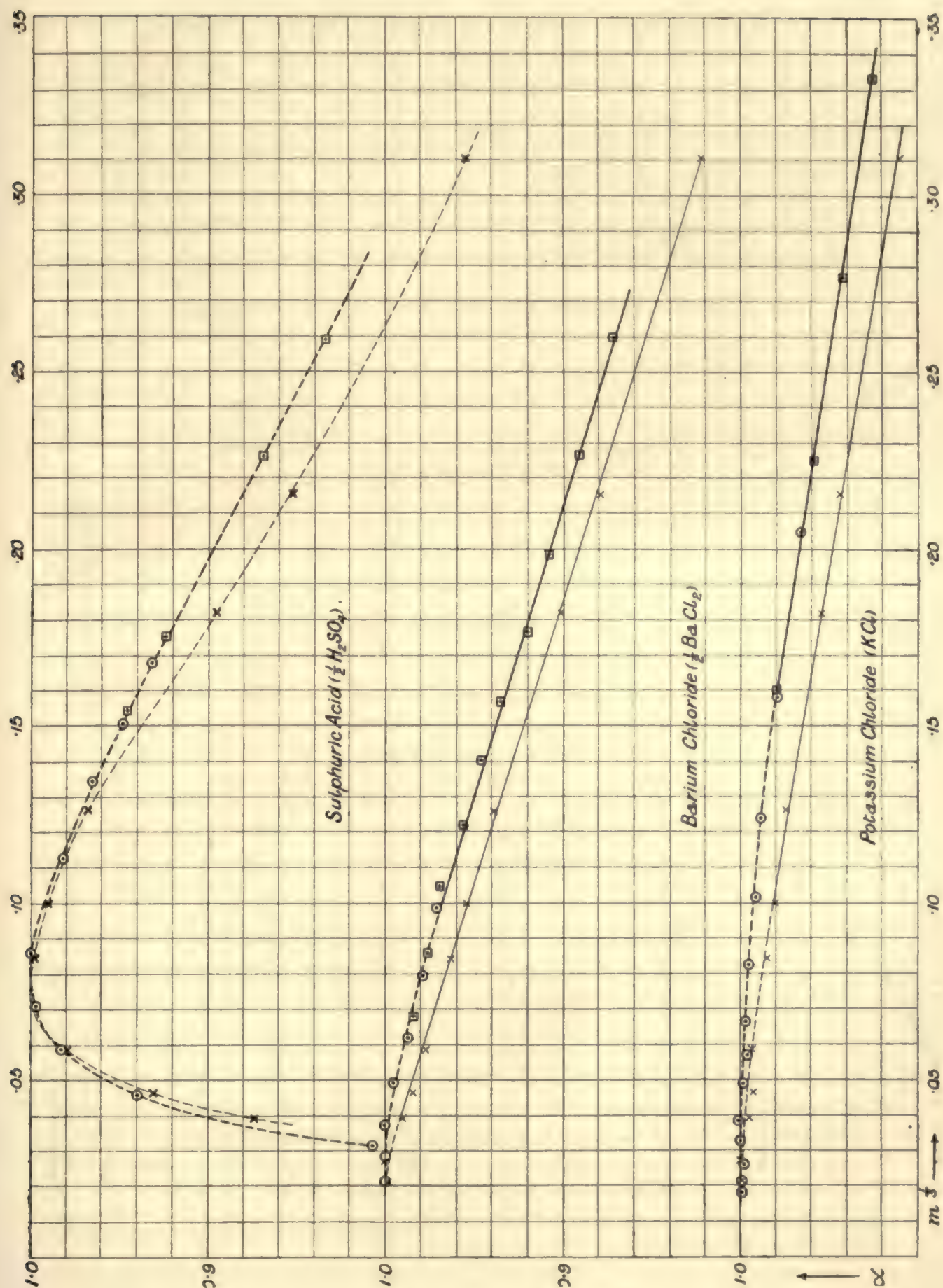
No.	m .	$m^{\frac{1}{2}}$.	R.	k/m .	α .
I.	7.791×10^{-6}	.0198	17424	3.576	.989
II.	1.604×10^{-5}	.0252	11535	3.535	.978
III.	3.174 "	.0317	7153	3.474	.961
IV.	6.181 "	.0395	4219	3.398	.940
V.	1.120×10^{-4}	.0482	2489	3.324	.920
VI.	2.191 "	.0603	1285	3.250	.899
VII.	4.598 "	.0772	670.7	3.177	.879
VIII.	8.662 "	.0953	362.6	3.150	.871
IX.	1.485×10^{-3}	.1141	213.4	3.136	.868
X.	2.366 "	.1333	134.6	3.127	.865
XI.	3.649 "	.1540	87.57	3.121	.863
XII.	5.327 "	.1746	60.10	3.118	.863
XIII.	7.338 "	.1943	43.90	3.100	.858
XIV.	9.990 "	.2154	32.20	3.106	.859
XV.	1.353×10^{-2}	.2383	23.88	3.092	.855
XVI.	1.784 "	.2613	18.28	3.065	.848

August 22, 1899. Solvent, $W = 219.32$. $R = 31280$.

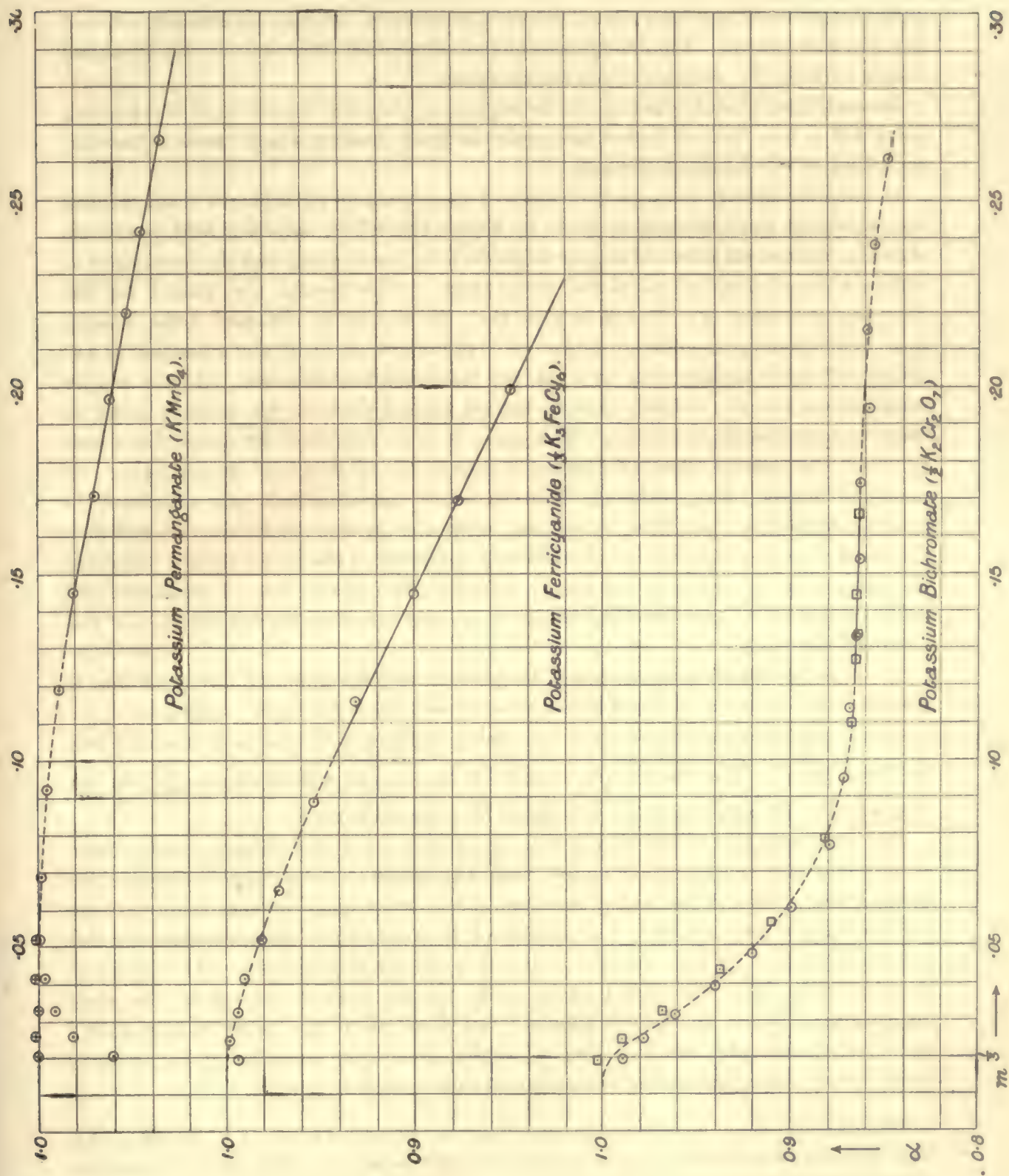
I.	7.374×10^{-6}	.0195	17050	3.619	1.002
II.	1.608×10^{-5}	.0252	11187	3.571	.989
III.	3.439 "	.0325	6575	3.496	.968
IV.	8.488 "	.0439	3134	3.382	.937
V.	1.844×10^{-4}	.0567	1568	3.285	.910
VI.	4.956 "	.0792	621.9	3.180	.881
VII.	1.333×10^{-3}	.1101	237.8	3.130	.867
VIII.	2.051 "	.1271	155.4	3.122	.865
IX.	2.399 "	.1339	132.99	3.120	.864
X.	3.023 "	.1446	105.52	3.124	.865
XI.	4.589 "	.1662	69.68	3.120	.864

SECTION 12.—Discussion of the Results.

The results of all these measurements are shown in a graphical form in the curves appended, the values of the ionizations observed being represented by dots surrounded by circles \odot . Wherever the observations could be connected by a ruled straight line,







a continuous mark has been made ; where the curvature becomes appreciable, a dotted line has been drawn. The divergences of individual observations from the smoothed curves indicate the probable errors of experiment.

Reasons have already been given for supposing that the ionization at the freezing point differs from that at higher temperatures by an amount which varies as the concentration of the solutions changes.

In order to directly compare the values of the ionization for different temperatures, the equivalent conductivities as given by KOHLRAUSCH* for sulphuric acid, potassium chloride, barium chloride and copper sulphate have been taken, and the ionizations at different concentrations calculated from them. The results are placed on the diagrams as crosses, \times . It will be seen that the curves so obtained differ in each case from those giving the results of the present work at 0° , the ionization at 18° falling off more rapidly than at 0° as the concentration increases. At the higher temperature, too, the dilution must be carried further than at the freezing point, in order to complete the ionization. This again is to be expected, for as we have seen (p. 323), the general effect of heating a solution is to decrease its ionization. It must be noticed that, although KOHLRAUSCH's concentrations are expressed in gramme-equivalents per litre of solution, while the present results are referred to a thousand grammes of solution, the difference produced in the curves by this difference in the method of reckoning is almost inappreciable ; in the case of sulphuric acid where it would be greatest, the change is invisible on the diagram till the last two solutions are reached.

In order to obtain a more direct comparison, and to eliminate any error due to difference of method, a series of measurements were made for copper sulphate at 18° in the present apparatus, the operations being conducted in precisely the same way as those at 0° . The results are shown by the crosses within circles \otimes in the diagram for that salt ; these are connected by a second curve.

It will be seen that, when this is done, the curves for 0° and 18° are nearly coincident while the concentration varies from the smallest value used to about $\cdot 001$ ($m^{\frac{1}{2}} = 0\cdot 10$). Beyond that value, the slant of the curve again becomes visibly greater for the higher temperature. The results of KOHLRAUSCH's measurements for this substance (also at 18°) are shown on the diagram by plain crosses. At very small concentrations they differ from those made by the present method at the same temperature by an appreciable amount ; but from about the point $m = 2 \times 10^{-3}$ ($m^{\frac{1}{2}} = \cdot 124$) onwards, the two sets of results practically coincide, giving a curve much below that representing the ionization at the freezing point.

* KOHLRAUSCH's latest lists of conductivities ('Ann. der Physik und Chem.,' N.F., vol. 66, p. 811, 1898) give the values as far as a maximum dilution of $\cdot 0001$ normal only. This is not far enough to directly estimate the value corresponding to complete ionization. The older numbers ('Wied. Ann.,' vol. 26, p. 195) are therefore used. They differ slightly in their absolute values from the new set, but this will not affect the ionization.

It seems, therefore, that for an accurate comparison with satisfactory freezing point determinations, it is, as we supposed, necessary to use measurements of conductivity made at 0° . This result justifies the amount of trouble and time expended on the present investigation, and the comparison with Mr. GRIFFITHS' promised measurements seems likely to give important information.

In comparing the diagrams for different substances, several results become evident. The normal type of curve is apparently that shown in the cases of potassium chloride, barium chloride, &c., in which the ionization increases as dilution proceeds and eventually reaches a maximum. On further dilution, the curve remains a horizontal straight line, and it therefore seems right to conclude that the ionization has become complete.

The abnormal shape of the curves for acids, observed when their conductivities are measured at 18° or 25° in glass vessels, is seen to still represent the facts when the conductivities are measured at 0° in platinum. At extreme dilution the equivalent conductivity falls off at a very rapid rate, and the cause of this fall, whatever it may be, is not removed by avoiding the use of glass or by taking the observations at the freezing point.

It has been usual to explain this phenomenon by action between the acid and the impurities present in the water; the result of the action being to reduce the effective quantity of acid in solution by an amount which becomes appreciable at great dilution, the substances formed having a smaller conductivity than the acid. The present experiments, however, seem to furnish a certain amount of evidence against this view.

The quantity of such impurity must be very small, and it is probable therefore that any action between it and the acid would be complete after the addition of the first quantity of acid, the amount of which must be large, reckoned in chemical equivalents, as compared with the total amount of impurity. Now, if the action were complete at the first addition of acid, it would be possible to correct the results of the other additions for the conductivity of that portion of the acid put out of action by the influence of the impurities on the first instalment. We ought to be able thus to get a curve agreeing in its general form with those of the normal type, which reach a maximum as the dilution is increased, and show no signs of falling off on further dilution. The conductivity of the first solution, when reduced in the usual way, gives a value for the ionization of $\cdot 809$. Let us calculate the conductivity required to raise this figure to $1\cdot 000$. It is $k = 11\cdot 29 \times m$, $11\cdot 29$ being the maximum value of k/m , corresponding to complete ionization (see p. 340), m is $3\cdot 254 \times 10^{-5}$, so that k should be $3\cdot 673 \times 10^{-4}$. It is, however, actually found to be $3\cdot 221 \times 10^{-4}$, so that the destruction of conductivity amounts to $\cdot 452 \times 10^{-4}$. Adding this value in the case of the second and following solutions, we get ionizations $1\cdot 006$, $1\cdot 016$, $1\cdot 017$, &c., numbers much too high to give a horizontal curve.

In this connection it is interesting to study the case of potassium permanganate. This salt is one which is particularly likely to react with the residual impurities of the

solvent, and the curve shows the same drop at extreme dilution as do the curves for acids, though in a less marked manner. But, in this case, a correction made on the lines indicated above gives the results :—

$$\begin{array}{lll} \alpha_1 = 1.000 & \alpha_2 = 1.002 & \alpha_3 = 1.000 \\ \alpha_4 = 1.002 & \alpha_5 = 1.001 & \alpha_6 = 0.999 \\ \alpha_7 = 0.996, \text{ \&c.} \end{array}$$

In this series the ionization of the first six solutions is constant, when corrected, to an accuracy of two parts in a thousand, which is within the limits of experimental error.

It is probable, therefore, that in the case of permanganate, the drop in the curve is caused by interaction between the salt and the residual impurities of the solvent, and that this action is completed by the first quantity of salt added. In the case of acids, however, some other explanation is needed.

This result is confirmed by another phenomenon which would not have been discovered if the usual method of beginning with a strong solution and diluting it had been adhered to.

When the first quantity of stock solution is added to the solvent and mixed with it, in the case of solutions having normal curves the resistance settles at once to its final value, but when the drop occurs in the ionization curve, the resistance is found to rise for some considerable time after mixing is complete, as though the action which caused the diminution in conductivity required time for its completion. This is illustrated by the following numbers :—

Barium Chloride.

Solution.	Time.	Temperature.	Resistance.
I.	6.41	.18	23000
	6.44	.18	22940
	6.47	.22	22900
	6.55	.24	22830

Copper Sulphate.

Solution.	Time.	Temperature.	Resistance.
I.	6.2	.00	18330
	6.6	.01	18280
	6.11	.02	18230

Potassium Permanganate.
1st Series.

Solution.	Time.	Temperature.	Resistance.
I.	11·10	·04	16590
	11·15	·05	16620
	11·22	·09	16640
	11·26	·11	16640
II.	11·34	·14	11610
	11·36	·13	11580
	11·40	·14	11570

2nd Series.

I.	12·27	·04	19550
	12·32	·05	19550
	12·41	·07	19580
	12·46	·10	19570
	12·48	·11	19560
II.	12·51	·14	12520
	12·54	·15	12520
	1·5	·17	12520

Sulphuric Acid.
1st Series.

Solution.	Time.	Temperature.	Resistance.
I.	5·24	·26	3060
	5·41	·33	3070
	5·45	·29	3075
	5·50	·32	3075
II.	5·53	·35	939·9
	5·57	·37	939·9
	6·7	·35	940·8
III.	6·12	·45	435·7
	6·14	·45	435·7

2nd Series.

I.	11·35	·12	9029
	11·40	·12	9047
	11·45	·12	9053
	12·4	·15	9060
II.	12·9	·20	3717
	12·25	·21	3718
III.	12·54	-0·01	687·9
	12·56	0·00	687·9

Thus the first solutions of substances like barium chloride and copper sulphate reach a constant resistance as soon as the measurements are begun, the slight decrease with time being caused by the slow rise of temperature which is going on. In the cases of potassium permanganate and sulphuric acid, however, the resistance goes on rising for nearly, or quite, half an hour after the first addition of stock solution is made. Potassium permanganate shows this phenomenon in the first solution only, the second one keeping constant or slowly decreasing in resistance just as do the solutions of normal salts, but in sulphuric acid it is appreciable in the second solution also. We are thus again led to the conclusion that the action with permanganate, whatever it may be, is completed by the first addition of salt, while a second addition of sulphuric acid is acted on in a similar manner to the first.

Experiments at higher temperatures have shown that this drop in the curve at extreme dilution occurs in the cases of acids, alkalies, and, to a smaller extent, of carbonates, which are unstable substances whose solutions probably contain a certain amount of alkali. Thus the phenomenon seems to be associated with the presence of hydrogen or hydroxyl ions, and to occur only in solutions which contain such ions.

Now these ions have two peculiarities. Firstly, they form the constituents of the solvent, water, in which the substances are dissolved; and, secondly, they are ions which travel in aqueous solutions with abnormally high velocities. These high velocities may, however, be connected with the existence of the ions in the solvent.

It is possible, in cases where one of the ions of a salt is much more mobile than the other, that the dilution of solution near the two electrodes, which we know to be the consequence of the movement of the ions, is so great at one electrode that the effective resistance of the liquid is increased, even in the small time during which the current flows in one direction. If this were the case we should expect that, in dilute solutions of acids where the equivalent conductivity has passed beyond the maximum, the measured resistance would depend on the rate of alternation of the current. Experiments made with such a solution of sulphuric acid showed that when the speed of the commutator was altered, the variation in resistance was inappreciable, just as it is in cases of other solutions.

Another possibility is that when one of the ions of the dissolved salt is also a constituent of the solvent, there is some action between them, whereby either the number of effective ions or their velocity is reduced. Such an action might require time to reach its completion, and hence is not inconsistent with the gradual rise in resistance which has been previously described. It is a well known fact that the amount of chemical dissociation is greatly reduced when one of the products is already present. Some such relation may explain the phenomenon in question.

The absolute values of the equivalent conductivities of potassium bichromate and potassium ferricyanide (see below) are, when calculated from the formulæ $\frac{1}{2}\text{K}_2\text{Cr}_2\text{O}_7$ and $\frac{1}{3}\text{K}_3\text{Fe}(\text{CN})_6$, higher than the numbers for any of the other salts used. It is unlikely that the complex anions of these substances should travel faster than simple

ions such as chlorine. Perhaps, therefore, solutions of these salts may contain a larger number of ions than we have assumed; thus, the ferricyanide may be resolved into potassium cyanide and ferric cyanide, when both K and Fe would behave as kations. The electrically equivalent weight would thus become half that taken above, the value of m would be doubled, and the equivalent conductivity reduced by one-half.

The curve giving the ionization of potassium bichromate is unlike any other. Beginning at extreme dilution, it first falls in a manner similar to that shown by curves for sulphates or other salts with divalent acids. As the concentration increases to a value of about 10^{-3} gramme-equivalent per litre, the ionization becomes nearly constant, and remains so till the concentration reaches about 10^{-2} gramme-equivalent, after which it again begins to fall, and almost looks as though it were passing into a new curve, the expression of a different chemical constitution. Perhaps these results may indicate that a change in the actual ions of the salt is brought about by increasing concentration. It is interesting to note that WALDEN* and OSTWALD† have already given evidence to show that bichromates in solution react with the water at moderate concentrations to form a mixture of the normal salt and acid.

Another point which may be of interest to chemists appears in the case of potassium permanganate. The slant of its curve is very small, and approximates to that for potassium chloride. It is much less than the slope for substances with divalent acid radicles such as sulphates. It is therefore probable that a molecule of potassium permanganate gives two ions, K and MnO_4' , and not three ions, represented by K' , K' , and $\text{Mn}_2\text{O}_8''$. The chemical structure of the salt in solution should then be represented by KMnO_4 . Mr. GRIFFITHS' freezing-point measurements may be expected to finally settle this question.

In order to collect the results of this investigation and exhibit them in a convenient form, the following tables have been compiled, showing the most probable values of the ionizations for certain definite concentrations. These results have been obtained from the smoothed curves, and three series of numbers have been tabulated.

In the first set, Table IX., the series of concentrations is the same as that used by KOHLRAUSCH, viz.: $m = 5, 2, 1 \times 10^{-2}$.

In the second set, Table X., OSTWALD'S series $m = 1, \frac{1}{2}, \frac{1}{4}$, &c., is taken.

In both these sets, m is measured in gramme-equivalents of solute per 1000 grammes of solution.

In the third set, Table XI., the concentrations are measured in terms of the number of gramme-molecules of solvent present to 1 gramme-molecule (not gramme-equivalent) of solute. The series taken for n is $5, 2, 1 \times 10^2$, the corresponding values of m being calculated by taking the molecular weight of water as 18, when $m = \frac{1000}{18 \times n}$ for potassium chloride, twice that number for barium chloride, &c.

* 'Zeits. f. physik. Chem.,' vol. 2, p. 73, 1888.

† *Ibid.*, vol. 2, p. 78, 1888.

For each set the numbers for $m^{\frac{1}{2}}$, corresponding to the concentrations used, were calculated, and the proper values of the ionization coefficients estimated from the smoothed curves.

Table XII. shows the approximate equivalent conductivities in absolute C.G.S. units. In order to obtain these numbers, a knowledge of the cell constant or "resistance capacity" of the apparatus is necessary. This knowledge is not needed for deducing the ionizations, and therefore no arrangements were made in planning the investigations for accurately obtaining it. Whenever the apparatus was dismantled for cleaning or other purposes, and set up again, it was found that a new measurement of the volume was necessary, slight differences in adjustment making the volume of water contained in it change by three or four-tenths of a cubic centimetre. Since a knowledge of the amount of solvent used is necessary for accurate estimation of the concentrations of the solutions, this redetermination of volume was always made. The variation in volume would involve a slight change in the cell constant of resistance, which, not being needed for the main purpose of the work, was only once determined. The conductivity of solutions of copper sulphate was, as already explained, measured at a temperature of 18° as well as at the freezing point, and a comparison could thus be made between the equivalent conductivity of solutions of known strength, as measured in the arbitrary cell units of this investigation, and the equivalent conductivity of solutions of the same strength as given by KOHLRAUSCH* in absolute units. Three values obtained for the conversion factor at three different concentrations were 2.345, 2.322 and 2.313, each multiplied by 10^{-11} , giving a mean cell constant of 2.327×10^{-11} . The variation between the three values depends on the slight difference in slant between the two curves for 18° , as shown in the diagram (p. 350).

This mean value of the cell constant was used for calculating the equivalent conductivities for all substances except potassium chloride, the greatest variations in the weight of water contained in the cell during these observations being from 219.25 to 219.61. Potassium chloride was investigated at an earlier date, before a change in arrangement had considerably altered the constant of the cell. In the case of this salt, however, KOHLRAUSCH has given equivalent conductivities for a few concentrations at 0° as well as at higher temperatures,† and thus a new determination of the cell constant was made, using a solution whose concentration was one hundredth normal. The constant was found to be 2.161×10^{-11} , and from this the absolute equivalent conductivities for the other concentrations of that salt were calculated from the present determinations of the ionization.

In conclusion I have to thank my wife for constant help, both with the experiments and calculations, Mr. E. H. GRIFFITHS for much assistance and many valuable suggestions, Mr. GREEN, for distilling a considerable part of the water used and

* 'Ann. der Physik und Chemie,' N.F., vol. 66, p. 813, 1898.

† 'Ann. der Physik und Chemie,' N.F., vol. 64, p. 441, 1898.

Mr. F. THOMAS for his skill and attention in constructing the apparatus. Professor J. J. THOMSON has made several temporary loans of apparatus from the Cavendish Laboratory, and Messrs. JOHNSON and MATTHEY lent the metal for the platinum still. Both the British Association and the Royal Society have made grants of money, without which the great cost of the apparatus would have rendered the investigation impossible.

TABLE IX.—Ionization Coefficients at 0°.

m = number of Gramme-equivalents of Solute per 1000 Grammes of Solution.

m .	$m^{\frac{1}{2}}$.	KCl.	$\frac{1}{2}$ BaCl ₂ .	$\frac{1}{2}$ H ₂ SO ₄ .	$\frac{1}{2}$ CuSO ₄ .	KMnO ₄ .	$\frac{1}{3}$ K ₃ FeCy ₆ .	$\frac{1}{2}$ K ₂ Cr ₂ O ₇ .
·00001	·0215	1·000	1·000	—	·998	1·000	·998	·991
·00002	·0272	1·000	1·000	—	·993	1·000	·996	·980
·00005	·0368	1·000	·998	·876	·981	1·000	·991	·952
·0001	·0464	·999	·995	·942	·967	1·000	·985	·929
·0002	·0585	·998	·990	·983	·947	·999	·977	·902
·0005	·0794	·996	·980	1·000	·908	·998	·961	·880
·001	·1000	·992	·969	·993	·863	·993	·944	·870
·002	·1260	·987	·953	·971	·807	·986	·919	·864
·005	·1710	·976	·925	·928	·717	·971	·876	·863
·01	·2154	·962	·896	·880	·638	·955	·834	·858
·015	·2466	·952	·876	·848	·591	·944	—	·853
·02	·2714	·944	·860	·822	·557	·934	—	—
·03	·3107	·932	·833	—	·509	—	—	—

TABLE X.—Ionization Coefficients at 0°.

m = number of Gramme-equivalents of Solute per 1000 Grammes of Solution.

m .	$m^{\frac{1}{2}}$.	KCl.	$\frac{1}{2}$ BaCl ₂ .	$\frac{1}{2}$ H ₂ SO ₄ .	$\frac{1}{2}$ CuSO ₄ .	KMnO ₄ .	$\frac{1}{3}$ K ₃ FeCy ₆ .	$\frac{1}{2}$ K ₂ Cr ₂ O ₇ .
$\frac{1}{131072}$	·0197	1·000	1·000	—	·999	1·000	·999	·994
$\frac{1}{65536}$	·0248	1·000	1·000	—	·997	1·000	·997	·985
$\frac{1}{32768}$	·0313	1·000	·999	·795	·988	1·000	·994	·969
$\frac{1}{16384}$	·0394	1·000	·997	·901	·978	1·000	·990	·947
$\frac{1}{8192}$	·0496	·999	·994	·954	·963	1·000	·983	·921
$\frac{1}{4096}$	·0625	·998	·988	·990	·940	·998	·974	·895
$\frac{1}{2048}$	·0788	·995	·980	1·000	·909	·996	·962	·880
$\frac{1}{1024}$	·0992	·992	·969	·993	·865	·993	·944	·870
$\frac{1}{512}$	·1250	·988	·954	·972	·809	·987	·920	·865
$\frac{1}{256}$	·1575	·979	·934	·941	·743	·977	·889	·863
$\frac{1}{128}$	·1984	·968	·908	·898	·666	·962	·850	·861
$\frac{1}{64}$	·2500	·951	·875	·844	·587	·942	—	·851
$\frac{1}{32}$	·3150	·930	·831	—	·505	—	—	—

TABLE XI.—Ionization Coefficients at 0°.

 n = number of Gramme-molecules of Solvent per Gramme-molecule of Solute.

n .	KCl.	BaCl ₂ .	H ₂ SO ₄ .	CuSO ₄ .	KMnO ₄ .	K ₃ FeCy ₆ .	K ₂ Cr ₂ O ₇ .
20,000,000	—	—	—	—	—	·998	—
10,000,000	—	1·000	—	·997	—	·997	·990
5,000,000	1·000	1·000	—	·992	1·000	·994	·976
2,000,000	1·000	·998	·890	·979	1·000	·987	·949
1,000,000	1·000	·994	·949	·965	1·000	·979	·925
500,000	·999	·989	·986	·944	1·000	·969	·901
200,000	·997	·979	1·000	·902	·999	·949	·878
100,000	·994	·966	·990	·856	·997	·926	·870
50,000	·992	·950	·967	·797	·993	·897	·866
20,000	·984	·922	·921	·705	·982	·846	·862
10,000	·974	·893	·872	·626	·969	—	·858
5,000	·960	·857	·813	·545	·952	—	—
2,000	·935	—	—	—	·923	—	—

TABLE XII.—Approximate Equivalent Conductivities at 0°. In C.G.S. Units $\times 10^{13}$. m = number of Gramme-equivalents of Solute per 1000 Grammes of Solution.

m .	KCl.	$\frac{1}{2}$ BaCl ₂ .	$\frac{1}{2}$ H ₂ SO ₄ .	$\frac{1}{2}$ CuSO ₄ .	KMnO ₄ .	$\frac{1}{3}$ K ₃ FeCy ₆ .	$\frac{1}{2}$ K ₂ Cr ₂ O ₇ .
·00001	807	765	—	704	756.	964	833
·00002	807	764	—	701	756	962	823
·00005	807	763	2309	692	756	957	800
·0001	806	761	2483	682	756	951	780
·0002	805	757	2591	668	755	943	758
·0005	804	750	2636	641	755	928	739
·001	800	741	2617	609	751	911	731
·002	796	729	2559	569	746	887	726
·005	787	708	2446	506	735	846	725
·01	776	685	2319	450	722	805	721
·015	768	671	2235	417	714	—	716
·02	761	658	2167	393	706	—	—
·03	752	638	—	359	—	—	—

IX. *Combinatorial Analysis. The Foundations of a New Theory.*

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Received March 19,—Read April 5, 1900.

INTRODUCTION.

IN the 'Transactions of the Cambridge Philosophical Society' (vol. 16, Part IV., p. 262), I brought forward a new instrument of research in Combinatorial Analysis, and applied it to the complete solution of the great problem of the "Latin Square," which had proved a stumbling block to mathematicians since the time of Euler. The method was equally successful in dealing with a general problem of which the Latin Square was but a particular case, and also with many other questions of a similar character. I propose now to submit the method to a close examination, to attempt to establish it firmly, and to ascertain the nature of the questions to which it may be successfully applied. We shall find that it is not merely an enumerating instrument but a powerful reciprocating instrument, from which a host of theorems of algebraical reciprocity can be obtained with facility.

We will suppose that combinations defined by certain laws of combination have to be enumerated; the method consists in designing, on the one hand, an operation and, on the other hand, a function in such manner that when the operation is performed upon the function a number results which enumerates the combinations. If this can be carried out we, in general, obtain far more than a single enumeration; we arrive at the point of actually representing graphically all the combinations under enumeration, and solve by the way many other problems which may be regarded as leading up to the problem under consideration. In the case of the Latin Square it was necessary to design the operation and the function the combination of which was competent to yield the solution of the problem. It is a much easier process, and from my present standpoint more scientific, to start by designing the operation and the function, and then to ascertain the questions which the combination is able to deal with.

§ 1.

Art. 1.—I will commence by taking the simplest possible question to which the method is applicable. Let us inquire into the number of permutations of n different letters. A knowledge of the result would at once lead us to design

An operation.	A function.
$(d/dx)^n$	x^n

since $(d/dx)^n x^n = n!$; but once we observe the way in which d/dx operates upon x^n we require no previous knowledge of the result to aid us in the design. Conceive x^n written as a product

$$\overset{xx}{xxxxnn} \dots$$

the operation of d/dx consists in substituting unity for x in all possible ways, and summing the results obtained.

$$\frac{d}{dx} x^n = 1.xxx \dots + x1xx \dots + xx1xx \dots + \dots = nx^{n-1}.$$

We have, in fact, to perform n operations of substitution; let us select one of these, say—

$$xx1xx \dots$$

and denote the minor operation, by which it has been obtained, by the scheme

		1 _a			...
--	--	----------------	--	--	-----

the suffix a denoting that the first operation of d/dx has resulted in the appearance of the unit.

To obtain $\frac{d}{dx}(xx1xx \dots)$ we have $n - 1$ minor operations by which x is replaced by unity in all possible ways. If one term obtained be

$$1x1xx \overset{x}{n} \dots$$

the operations by which this has been reached may be denoted by the scheme

		1 _a			...
1 _b					...

and by proceeding in this manner we finally reach a lattice, square and of n^2 compartments, which is the diagrammatic representation of one of the $n!$ combinations of minor operations which results from the operation of $(d/dx)^n$ upon x^n . If we transfer the $1_b, 1_c, \dots$ to the top row we see that to each diagram corresponds a permutation of the n different letters a, b, c, \dots . Moreover suppressing the letters a, b, c, \dots we see that we have solved the following problem, viz. :—To place n units in the compartments of the square of order n , so that each row and each column contains one and only one unit. In general we find that the problems that can be solved have some simple definition upon a lattice, as in the present instance. Writing a, b, c, \dots as a_1, a_2, a_3, \dots the suffix of the letter is given by the row and the place in the permutation by the column, so that to a_3 standing t^{th} in a permutation would correspond a unit in the s^{th} row and t^{th} column of the lattice.

It may be remarked, and will afterwards appear, that in general many different designs of operation and function are appropriate to a particular problem.

Art. 2.—With the immediate object of applying the method to the general case of permutation, there being any number of identities of letters, we must first obtain another solution of the foregoing problem.

Let $\alpha_1, \alpha_2, \alpha_3 \dots$ be a number of quantities and a_1, a_2, a_3, \dots their elementary symmetric functions. Further, let

$$d_1 = D_1 = \frac{d}{da_1} + a_1 \frac{d}{da_2} + a_2 \frac{d}{da_3} \dots$$

and $a_s = \Sigma \alpha_1 \alpha_2 \dots \alpha_s = (1')$ in partition notation.

We may take as operation and function

$$D_1^n \text{ and } (1)^n,$$

equivalent to $(d/da_1)^n$ and α_1^n , which we had before, but more convenient as being readily generalisable.

Let $D_s = \frac{1}{s!} d_1^s$, d_1^s denoting an operator of order s , obtained by symbolical multiplication as in Taylor's theorem. Suppose the question be the enumeration of the permutations of the quantities in $\alpha_1^{\pi_1} \alpha_2^{\pi_2} \dots \alpha_n^{\pi_n}$, where $\Sigma \pi = n$. I say that the operation and function are respectively

$$D_{\pi_1} D_{\pi_2} \dots D_{\pi_n} \text{ and } (1)^n.$$

Observe that this is merely the multinomial theorem for

$$\begin{aligned} (1)^n &= \dots + \frac{n!}{\pi_1! \pi_2! \dots \pi_n!} \Sigma \alpha_1^{\pi_1} \alpha_2^{\pi_2} \dots \alpha_n^{\pi_n} + \dots \\ &= \dots + \frac{n!}{\pi_1! \pi_2! \dots \pi_n!} (\pi_1 \pi_2 \dots \pi_n) + \dots \end{aligned}$$

in partition notation; and

$$D_{\pi_1} D_{\pi_2} D_{\pi_3} \dots D_{\pi_n} (\pi_1 \pi_2 \dots \pi_n) = 1.*$$

Hence

$$D_{\pi_1} D_{\pi_2} D_{\pi_3} \dots D_{\pi_n} (1)^n = \frac{n!}{\pi_1! \pi_2! \pi_3! \dots \pi_n!}$$

the result we require.

The important operator D_π has been discussed by the author.† Its effect upon a monomial symmetric function is to erase a part π from the partition expression of the function.

Thus

$$D_\pi \Sigma \alpha^r \beta^s \gamma^t \dots = D_\pi (\pi \rho \sigma \dots) = (\rho \sigma \dots) = \Sigma \alpha^r \beta^s \dots$$

* See HAMMOND, 'Proc. Lond. Math. Soc.,' vol. 13, p. 79; also 'Trans. Camb. Phil. Soc.,' *loc. cit.*

† 'Messenger of Mathematics,' vol. 14, p. 164. 'American Journal of Mathematics,' "Third Memoir on a New Theory of Symmetric Functions," vol. 13, p. 8 *et seq.*, p. 34 *et seq.* 'Trans. Camb. Phil. Soc.,' vol. 16, part IV., p. 262.

If no part π presents itself in the operand, D_π causes the monomial function to vanish. Thus

$$D_\pi(\rho\sigma\tau \dots) = 0.$$

The compound operation $D_{\pi_1}D_{\pi_2}D_{\pi_3} \dots$ denotes the *successive* performance of the operations

$$D_{\pi_1}, D_{\pi_2}, D_{\pi_3}, \dots \text{ of orders } \pi_1, \pi_2, \pi_3, \dots \text{ respectively.}$$

The law of operation of D_π establishes that the component operations $D_{\pi_1}, D_{\pi_2}, D_{\pi_3}, \dots$ may be performed *in any order*. Thus

$$D_\pi D_{\pi_2}(\pi_1\pi_2\rho\sigma \dots) = D_{\pi_1}(\pi_1\rho\sigma \dots) = D_{\pi_2}(\pi_2\rho\sigma \dots) = (\rho\sigma \dots).$$

As the order of operation is immaterial, it is found convenient in most cases to operate with $D_{\pi_1}D_{\pi_2}D_{\pi_3} \dots$ in the order $D_{\pi_1}, D_{\pi_2}, D_{\pi_3}, \dots$; this may seem at first sight at variance with the ordinary usage in the Differential Calculus, but there is a convenience in ordering the operator from left to right in agreement with the practice of ordering a partition from left to right. If, further, we note the result—

$$D_\pi(\pi) = 1$$

we have a complete account of the operator so far as it is concerned with an operand, which is merely a monomial symmetric function. The operation of D_π upon a symmetric function product is of even greater importance in the present theory. It has the effect of erasing a partition of π from the product, one part from each factor, in all possible ways; the result of the operation being a sum of products, one product arising from each such erasure of a partition. This has been set forth at length in the papers to which reference has been given, but in deference to the suggestion of one of the Referees appointed by the Royal Society to report upon the present paper, a number of examples are given to familiarise readers with the processes which are so much employed in what follows.

Example 1.—Consider

$$D_\pi(1)^n.$$

The operand consists of n factors, each of which is (1) ; the operator D_π is performed through the partition of the number π which involves π units; this partition must be erased from $(1)^n = (1)(1)(1) \dots$ to n factors in each of the $\binom{n}{\pi}$ possible ways, and the results added. Thus

$$D_\pi(1)^n = \binom{n}{\pi}(1)^{n-\pi}.$$

As a particular case

$$\begin{aligned} D_2(1)^4 &= (1)(1)(1)(1) + (1)(1)(1)(1) + (1)(1)(1)(1) + (1)(1)(1)(1) \\ &\quad + (1)(1)(1)(1) + (1)(1)(1)(1) = 6(1)^2 = \binom{4}{2}(1)^2. \end{aligned}$$

This, the simplest example that could be taken, shows clearly the great value of the operator D_π as an instrument in combinatorial analysis.

Example 2.—It follows from the first example that if $\Sigma \pi = n$,

$$D_{\pi_1} D_{\pi_2} D_{\pi_3} \dots D_{\pi_n} (1)^n = \frac{n!}{\pi_1! \pi_2! \pi_3! \dots \pi_n!}.$$

Example 3.—Consider

$$D_4 (2)^2 (1)^2.$$

We are concerned with the partitions of the number 4 into 2,2 and 2,1,1, and

$$D_4 (2) (2) (1) (1) = (2)(2)(1)(1) + (2)(2)(1)(1) + (2)(2)(1)(1) = (1)^2 + 2(2).$$

If now we operate with D_2 we have to take account of the partitions 1,1 and 2 of the number 2, and we find

$$D_4 D_2 (2)^2 (1)^2 = (1)(1) + 2(2) = 3,$$

and we have the result

$$(2)^2 (1)^2 = \dots + 3(42) + \dots$$

as a consequence.

Similarly, reversing the order of the operations

$$D_2 (2) (2) (1) (1) = 2(2)(1)(1) + (2)(2) \quad \text{and} \quad D_4 (2) (1) (1) = D_4 (2) (2) = 1,$$

verifying the previous result.

If no partition of π can be picked out in this way from the partitions of the functions forming the product, the result of the operation is zero.

Example 4.—

$$D_2 (1^2)^2 = D_2 (1^2) (1^2) = (1)(1) = (1)^2.$$

It is important to notice here that a unit is erased from $(1^2) = (11)$ in *only one way*, and that for present purposes a number of similar figures enclosed in a bracket are to be considered as the same, and not different; we have already seen that when the figures are similar, but in different brackets, they are, for the purpose of selection, to be considered as different figures.

Observe that since

$$D_2 (1^2)^2 = (1)^2 = (2) + 2(1^2),$$

we may say that

$$(1^2)^2 = (2^2) + 2(21^2) + \dots,$$

the terms to be added on the right for the full expression being such as do not contain a figure 2.

To obtain the lattice representations, suppose $\pi_1, \pi_2, \pi_3, \dots, \pi_n$ to be in descending order, and thus to be an ordered partition of the number n .

Since $D_{\pi_1}(1)^n = \binom{n}{\pi_1}(1)^{n-\pi_1}$, D_{π_1} may be regarded as breaking up into $\binom{n}{\pi_1}$ minor operations, each of which consists in erasing π_1 of the n factors

$$(1)(1)(1) \dots (1),$$

and replacing them by units. On the diagram we denote one such minor operation by (say),

1	1	.	1	.	1	1	.	.	.
---	---	---	---	---	---	---	---	---	---

----n° of units = π_1 ,

Keeping to this term,

$$1.1.(1).1.(1).1.1.(.1)(1) \dots$$

and operating with D_{π_2} , we find the operation breaking up into $\binom{n-\pi_1}{\pi_2}$ minor operations, each of which consists in erasing π_2 of the factors, and replacing them by units. Selecting one of these minor operations, we find that the corresponding term has been obtained by operations conforming to the diagram of two rows

1	1	.	1	.	1	1	.	.	.
.	.	1	.	.	.	1	1	.	.

----n° of units = π_1 ,
----n° of units = π_2

Proceeding in this manner, we finally arrive at a lattice of n rows and n columns, such that there is one and only one unit in each column, while the numbers of units in the 1st, 2nd . . . n th rows are $\pi_1, \pi_2, \dots, \pi_n$ respectively.

We have thus the associated problem on the lattice, and we obtain $\frac{n!}{\pi_1! \pi_2! \dots \pi_n!}$ representations on the lattice corresponding to the permutations of the quantities in $\alpha_1^{\pi_1} \alpha_2^{\pi_2} \dots \alpha_n^{\pi_n}$.

The simple introductory examples lead one to expect that the method will be found capable of dealing with questions either of a chess board character or which are concerned with rectangular lattices. Further, the idea of lattice rotation gives promise of leading to theorems of algebraic reciprocity and of reciprocity in the theory of numbers, features almost inseparable from any lattice theory.

Art. 3.—*The graph of a partition.*—It is convenient to have before us the connexion between this theory and the SYLVESTER-FERRERS graph of a unipartite partition.

Consider the operation $D_3 D_2^2 D_1$ and the symmetric function $(1^4)(1^3)(1)$, $(32^3 1)$ being the partition conjugate to (431) .

$D_3 D_2^2 D_1 (1^4)(1^3)(1) = D_2^2 D_1 (1^3)(1^2)$, the operation D_3 erasing one part, viz.: unity from each factor; this we denote as usual by

$$\boxed{1} \boxed{1} \boxed{1} ;$$

again $D_2^2 D_1 (1^3) (1^2) = D_2 D_1 (1^2) (1)$ and the two operations together give us

1	1	1
1	1	

and $D_2 D_1 (1^2) (1) = D_1 (1) = 1$ and the complete lattice representation is

1	1	1
1	1	
1	1	
1		

which is none other than the graph of the partition (32^21) or of (431) according as it is read by rows or by columns. We might also have operated with $D_4 D_3 D_1$ upon $(1^3) (1^2)^2 (1)$ and, in general, if $(\pi_1 \pi_2 \pi_3 \dots)$, $(\rho_1 \rho_2 \rho_3 \dots)$ be conjugate partitions, we obtain their graphs either by operating with $D_{\pi_1} D_{\pi_2} D_{\pi_3} \dots$ upon $(1^{\pi_1}) (1^{\pi_2}) (1^{\pi_3}) \dots$ or with $D_{\rho_1} D_{\rho_2} D_{\rho_3} \dots$ upon $(1^{\rho_1}) (1^{\rho_2}) (1^{\rho_3}) \dots$

Art. 4.—I proceed to consider some less obvious but equally interesting examples of the method. The diagrams obtained depend upon the law by which the operation is performed upon the function which is the operand. The operator D_{π} in connexion with symmetric function operands is of commanding importance. It would be difficult to imagine an operation better adapted to research in combinatorial analysis. We shall find later that an analogous operation exists which can be employed when symmetric functions of several systems of quantities are taken as operands. As an example of diagram formation, take as operator $D_4 D_3^2$ and as function $(3) (21) (2) (1) (1)$ the weight of operator and of function being the same.

We have

$$\begin{aligned}
 & D_4(3)(21)(2)(1)(1) \\
 &= (.) (2.) (2) (1) (1) + (.) (21) (2) (.) (1) + (.) (21) (2) (1) (.) \\
 &\quad + (3) (.) (1) (.) (1) (1) \\
 &\quad + (3) (.) (1) (2) (.) (.) + (3) (2.) (.) (1) (.) + (3) (2.) (.) (.) (1) \\
 &\quad + (3) (21) (.) (.) (.),
 \end{aligned}$$

the eight terms arising from the partitions 31, 22, 211 of the number 4. The dots take the place of the picked out partitions.

Hence

$$\begin{aligned}
 & D_4(3)(21)(2)(1)(1) \\
 &= (2)^2(1)^2 + 2(21)(2)(1) + (3)(1)^3 + 3(3)(2)(1) + (3)(21).
 \end{aligned}$$

The operation D_4 breaks up here into eight minor operations; taking any one of

these—say that one which consists in taking 3 from the factor (3), and 1 from the factor (21), we form the first row of our diagram, viz.:—

3	1			
---	---	--	--	--

The term resulting from the selected minor operation is

$$(\cdot)(2)(2)(1)(1);$$

the operation of D_3 results in four minor operations corresponding to the four ways of picking out a 2 and a 1 from different factors; we may select the particular minor operation which results in

$$(\cdot)(\cdot)(2)(1)(\cdot),$$

and now we add on the second row which denotes this minor operation, and obtain the diagram of two rows.

3	1			
	2			1

We can now only operate in one way with D_3 upon $(\cdot)(\cdot)(2)(1)(\cdot)$ and we finally obtain the diagram of three rows:—

3	1			
	2			1
		2	1	

which possesses the property that the sums of the numbers in the successive rows are 4, 3, 3, respectively, while the successive columns involve the partitions (3), (21), (2), (1), (1) respectively.

The number of such diagrams is A where

$$(3)(21)(2)(1)^2 = \dots + A(43^2) + \dots,$$

and A has the analytical expression

$$D_4 D_3^2 (3)(21)(2)(1)^2.$$

Let us now consider the problem of placing units in the compartments of a lattice of m rows and l columns, not more than one unit in each compartment, in such wise that we can count $\mu_1, \mu_2, \dots, \mu_m$ units in the successive rows, and $\lambda_1, \lambda_2, \dots, \lambda_l$ units in the successive columns. Take

As operation.

As function.

$$D_{\mu_1} D_{\mu_2} \dots D_{\mu_m} \quad \text{and} \quad (1^{\lambda_1})(1^{\lambda_2}) \dots (1^{\lambda_l}).$$

If

$$(1^{\lambda_1})(1^{\lambda_2}) \dots (1^{\lambda_l}) = \dots + A(\mu_1 \mu_2 \dots \mu_m) + \dots$$

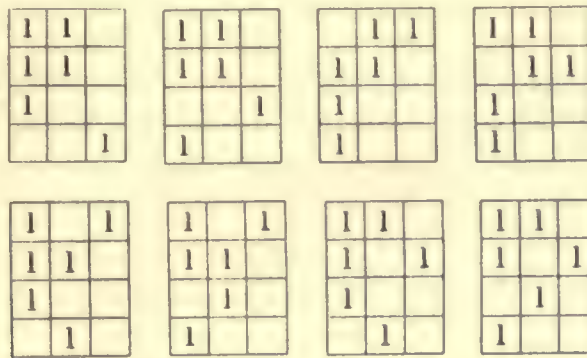
$$D_{\mu_1} D_{\mu_2} \dots D_{\mu_m} (1^{\lambda_1})(1^{\lambda_2}) \dots (1^{\lambda_l}) = A,$$

and we can show that the number A enumerates the lattices under investigation. The operation D_{μ_1} makes selections of every μ_1 of the l factors and erases a part unity from each; one minor operation of D_{μ_1} therefore is denoted by μ_1 units placed in μ_1 compartments of the first row of a lattice of l rows; the operation D_{μ_2} adds on a second row, in which units appear in μ_2 of the compartments, and so on we finally arrive at a lattice possessing the desired property as regards rows, and as obviously the column property obtains, the problem is solved.

Ex. gr. Take $\lambda_1 = 3, \lambda_2 = 2, \lambda_3 = 1, \mu_1 = 2, \mu_2 = 2, \mu_3 = 1, \mu_4 = 1$

$$(1^3)(1^2)(1) = a_3 a_2 a_1 = \dots + 8(2211) + \dots$$

The eight diagrams are



and no others possess the desired property.

We can now apply the method so as to be an instrument of reciprocation in algebra. If we transpose the diagrams so as to read by rows as they formerly did by columns, the effect is to interchange the set of numbers $\lambda_1, \lambda_2, \dots, \lambda_l$ with the set $\mu_1, \mu_2, \dots, \mu_m$, and the number of diagrams is not altered. Hence the reciprocal theorem.

$$\begin{aligned} \text{If} \quad & (1^{\lambda_1})(1^{\lambda_2}) \dots (1^{\lambda_l}) = \dots + A(\mu_1 \mu_2 \dots \mu_m) + \dots \\ \text{then} \quad & (1^{\mu_1})(1^{\mu_2}) \dots (1^{\mu_m}) = \dots + A(\lambda_1 \lambda_2 \dots \lambda_l) + \dots \end{aligned}$$

a theorem known to algebraists as the Cayley-Betti Law of Symmetry in Symmetric Functions.

The easy intuitive nature of this proof of the theorem is very remarkable.

Art. 5.—In the above the magnitude of the numbers, appearing in the compartments of the lattice, has been restricted so as not to exceed unity. This restriction may be removed in the following manner. Consider the symmetric functions known as the homogeneous product sums of the quantities $\alpha_1, \alpha_2, \alpha_3, \dots$ viz.—

$$\begin{aligned} h_1 &= (1), \\ h_2 &= (2) + (1^2), \\ h_3 &= (3) + (21) + (1^3), \\ &\dots \end{aligned}$$

and note the result

$$D_s h_\lambda = h_{\lambda-s},$$

and also

$$D_s h_{\lambda_1} h_{\lambda_2} \dots h_{\lambda_l} = \Sigma h_{\lambda_1-\sigma_1} h_{\lambda_2-\sigma_2} h_{\lambda_3-\sigma_3} \dots h_{\lambda_l-\sigma_l}$$

where $(\sigma_1 \sigma_2 \sigma_3 \dots \sigma_l)$ is a partition of s and the sum is for all such partitions, and for a particular partition is for all ways of operating upon the suffixes with the parts of the partition. Thus

$$\begin{aligned} D_3 h_\lambda h_\mu h_\nu &= h_{\lambda-3} h_\mu h_\nu + h_\lambda h_{\mu-3} h_\nu + h_\lambda h_\mu h_{\nu-3} \\ &+ h_{\lambda-2} h_{\mu-1} h_\nu + h_\lambda h_{\mu-2} h_{\nu-1} + h_{\lambda-1} h_\mu h_{\nu-2} \\ &+ h_{\lambda-1} h_{\mu-2} h_\nu + h_\lambda h_{\mu-1} h_{\nu-2} + h_{\lambda-2} h_\mu h_{\nu-1} \\ &+ h_{\lambda-1} h_{\mu-1} h_{\nu-1}. \end{aligned}$$

If from the result of $D_s h_{\lambda_1} h_{\lambda_2} \dots h_{\lambda_l}$ we select the term product $h_{\lambda_1-\sigma_1} h_{\lambda_2-\sigma_2} \dots h_{\lambda_l-\sigma_l}$, the corresponding lattice will have as first row

$$\begin{array}{|c|c|c|c|} \hline \sigma_1 & \sigma_2 & \sigma_3 & \sigma_4 \\ \hline \end{array} \dots \begin{array}{|c|} \hline \sigma_l \\ \hline \end{array}$$

the sum of the numbers being s , and if in the selected product we now operate with D_t we can select a term product from the result, and the two minor operations may be indicated by the two-row lattice,

$$\begin{array}{|c|c|c|c|} \hline \sigma_1 & \sigma_2 & \sigma_3 & \sigma_4 \\ \hline \tau_1 & \tau_2 & \tau_3 & \tau_4 \\ \hline \end{array} \dots \begin{array}{|c|} \hline \sigma_l \\ \hline \tau_l \\ \hline \end{array}$$

the sum of the numbers τ being t .

Hence if we take as operation

$$D_{\mu_1} D_{\mu_2} \dots D_{\mu_m},$$

and as function

$$h_{\lambda_1} h_{\lambda_2} \dots h_{\lambda_l},$$

we will obtain a number of lattices of m rows and l columns, which possess the property that the sums of the numbers in the successive rows are $\mu_1, \mu_2, \dots, \mu_m$, and in the successive columns $\lambda_1, \lambda_2, \dots, \lambda_l$, no restriction being placed upon the magnitude of the numbers. The number of such lattices is A , where

$$h_{\lambda_1} h_{\lambda_2} \dots h_{\lambda_l} = \dots + A(\mu_1 \mu_2 \dots \mu_m) + \dots$$

and now transposition of lattices shows that

$$h_{\mu_1} h_{\mu_2} \dots h_{\mu_m} = \dots + A(\lambda_1 \lambda_2 \dots \lambda_l) + \dots$$

yielding a proof of a law of symmetry discovered by the present author many years ago. The process involves the actual formation of the things enumerated by the number A . The secret of its success in this instance lies in the result $D_\lambda h_s = h_{s-\lambda}$.

Ex. gr. We have

$$D_2^2 D_1^2 h_3 h_2 h_1 = 18$$

$$i.e. \quad h_3 h_2 h_1 = \dots + 18(2211) + \dots$$

$$h_2^2 h_1^2 = \dots + 18(321) + \dots$$

and we must have 18 lattices; now eight of these, in which the compartment numbers do not exceed unity, have been depicted above; the remaining 10 are

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Art. 6.—The next problem I will consider is that in which the magnitude of the compartment numbers has a superior limit k .

Let k_s denote the homogeneous product sum of order s in which none of the quantities $\alpha_1, \alpha_2, \alpha_3, \dots$ is raised to a higher power than k . *Ex. gr.* If $k = 2$, k_3 will be $(21) + (1^3)$, and not $(3) + (21) + (1^3)$.

We have $D_\lambda k_s = k_{s-\lambda}$ where $\lambda \equiv k$,

and $D_\lambda k_s = 0$ if $\lambda > k$.

Take as operation

$$D_{\mu_1} D_{\mu_2} \dots D_{\mu_m}$$

and as function $k_{\lambda_1}, k_{\lambda_2}, \dots, k_{\lambda_l}$, and we will obtain a number of lattices of m rows and l columns which possess the property that the sums of the numbers in the successive rows are $\mu_1, \mu_2, \dots, \mu_m$, and in the successive columns $\lambda_1, \lambda_2, \dots, \lambda_l$, the magnitude of the compartment numbers being restricted not to exceed k .

The number of such lattices is

$$D_{\mu_1} D_{\mu_2} \dots D_{\mu_m} k_{\lambda_1} k_{\lambda_2} \dots k_{\lambda_l} = A,$$

where $k_{\lambda_1} k_{\lambda_2} \dots k_{\lambda_l} = \dots + A(\mu_1 \mu_2 \dots \mu_m) + \dots$,

and by transposing the lattices

$$k_{\mu_1} k_{\mu_2} \dots k_{\mu_m} = \dots + A(\lambda_1 \lambda_2 \dots \lambda_l) + \dots;$$

establishing a law of symmetry in symmetrical algebra.

I observe that if $k = 9$, the lattices associated with and enumerated by

$$D_{15}^3 k_{15}^3$$

include all the row and column-magic squares connected with the natural series of numbers 1, 2, 3, 4, 5, 6, 7, 8, 9. In general if $N = \frac{1}{2}n(n^2 + 1)$, the lattices enumerated by $D_N^* k_N^*$, where $k = n^2$, include all the magic squares of order n connected with the first n^2 numbers. If we could further impress the condition that no compartment number is to be twice repeated, we would be successful in enumerating the magic squares divorced from the diagonal property. This seems to be a matter of difficulty, which is increased if an attempt be made to introduce diagonal and other conditions to which certain classes of magic squares are subject.

It may be gathered from what has been said, that every case of symmetric function multiplication is connected with a theory of lattice combinations. For if we take as function

$$(\lambda_1 \mu_1 \nu_1 \dots) (\lambda_2 \mu_2 \nu_2 \dots) \dots (\lambda_s \mu_s \nu_s \dots),$$

and as operation

$$D_p D_q D_r \dots,$$

where

$$p + q + r + \dots = \Sigma \lambda + \Sigma \mu + \Sigma \nu + \dots,$$

we have

$$D_p D_q D_r \dots (\lambda_1 \mu_1 \nu_1 \dots) ((\lambda_2 \mu_2 \nu_2 \dots) (\dots) \dots (\lambda_s \mu_s \nu_s \dots)) = A,$$

where

$$(\lambda_1 \mu_1 \nu_1 \dots) (\lambda_2 \mu_2 \nu_2 \dots) \dots (\lambda_s \mu_s \nu_s \dots) = \dots + A(pqr \dots) + \dots;$$

that is to say, we multiply together a number of monomial symmetric functions so as to exhibit it as a sum of monomial functions; in this sum we find a particular monomial function affected with a numerical coefficient A which, as shown by the present theory, is the number which enumerates lattices of a certain class easily definable. Thus, in the present instance, if the partition $(pqr \dots)$ involve t parts, the lattices have s columns and t rows; the operation D_p acts, through its various partitions, upon the product of monomials, and any mode of picking out a partition of p from the factors of the product, one part from each factor, constitutes a minor operation which yields the first row of a lattice; the operation D_q is similarly responsible for all the second rows of the lattices, and finally every resulting lattice possesses a property which may be defined as under:—

The numbers in the successive rows are partitions of the numbers p, q, r, \dots respectively, and in the successive columns are the partitions $(\lambda_1 \mu_1 \nu_1 \dots)$, $(\lambda_2 \mu_2 \nu_2 \dots)$, \dots , $(\lambda_s \mu_s \nu_s \dots)$ respectively. Such are the lattices enumerated by the number A . One is reminded somewhat of CAYLEY'S well-known algorithm for symmetric function multiplication (invented by him for use in his researches in the

theory of Invariants), but here the determination is representative as well as enumerative, and has moreover analytical expression.

Ex. gr. Take as function (987)(654)(321), and as operation $D_{13}D_{15}D_{17}$; then

$$D_{13}D_{15}D_{17}(987)(654)(321) = A,$$

$$\text{where} \quad (987)(654)(321) = \dots + A(13.15.17) + \dots$$

One of the associated lattices is

7	5	1
8	4	3
9	6	2

where observe that the numbers in the successive rows constitute partitions of the numbers 13, 15, 17 respectively, whilst in the successive columns the numbers constitute the partitions (987), (654), (321) respectively. The number of lattices possessing this property, is A, and A is readily found to have the value 6. If we had to find an expression for the number of row and column-magic squares of order 3, it would be necessary to write down the sum of all products

$$(762)(951)(843)$$

formed from the first 9 ($=n^2$) numbers in such wise that the content of each partition factor is $15 = \frac{1}{2}n(n^2 + 1)$, attention being paid to the order of the partitions, and to take as operation D_{15}^3 or in general $D_{\frac{1}{2}n(n^2+1)}^n$. The resulting lattices will all be magic squares in which the diagonal property is not essential, and the result of the operation upon the function will give the enumerating number.

Art. 7. To resume; in the lattice compartments we find invariably the numbers $\lambda_1, \mu_1, \nu_1, \dots, \lambda_2, \mu_2, \nu_2, \dots, \lambda_s, \mu_s, \nu_s, \dots$ such numbers being subject to certain conditions for each row and each column. The assemblages of numbers in the successive columns do not vary from lattice to lattice, but those in the successive rows do vary from lattice to lattice.

$$\begin{aligned} \text{Let} \quad \lambda_1 + \mu_1 + \nu_1 + \dots &= \lambda; \quad \lambda_2 + \mu_2 + \nu_2 + \dots = \mu; \\ \lambda_3 + \mu_3 + \nu_3 + \dots &= \nu, \text{ \&c. } \dots \end{aligned}$$

Then we have the following facts:—

- (i.) The whole assemblage of numbers, $\lambda_1, \mu_1, \nu_1, \dots, \lambda_2, \mu_2, \nu_2, \dots, \lambda_3, \mu_3, \nu_3, \dots$ is unaltered from lattice to lattice.
- (ii.) The numbers λ, μ, ν, \dots appertaining to the columns, and the numbers p_1, q_1, r, \dots appertaining to the rows, are unaltered from lattice to lattice.

These conditions do not define the lattices in question, because other lattices comply with them, viz., those in which, the whole assemblages of compartment numbers remaining unchanged, the column partitions, while satisfying the condition (ii.), are other than

successively.
 $(\lambda_1 \mu_1 \nu_1 \dots), (\lambda_2 \mu_2 \nu_2 \dots), (\lambda_3 \mu_3 \nu_3 \dots), \dots$

Let

$$\begin{aligned}\lambda_1' + \mu_1' + \nu_1' + \dots &= \lambda, \\ \lambda_2' + \mu_2' + \nu_2' + \dots &= \mu, \\ \lambda_3' + \mu_3' + \nu_3' + \dots &= \nu, \\ &\dots\end{aligned}$$

the assemblage of dashed numbers being in some order identical with the assemblages of undashed numbers. The new conditions include lattices enumerated by

$$D_{pqr} \dots (\lambda_1' \mu_1' \nu_1' \dots) (\lambda_2' \mu_2' \nu_2' \dots) (\lambda_3' \mu_3' \nu_3' \dots) \dots$$

and the totality of lattices, implied by them, is enumerated by

$$D_{pqr} \dots \Sigma (\lambda_1' \mu_1' \nu_1' \dots) (\lambda_2' \mu_2' \nu_2' \dots) (\lambda_3' \mu_3' \nu_3' \dots) \dots$$

the summation being for every separation of the assemblage of numbers

$$\lambda_1, \mu_1, \nu_1, \dots, \lambda_2, \mu_2, \nu_2, \dots, \lambda_3, \mu_3, \nu_3, \dots$$

into partitions

$$(\lambda_1' \mu_1' \nu_1' \dots), (\lambda_2' \mu_2' \nu_2' \dots), (\lambda_3' \mu_3' \nu_3' \dots), \dots$$

such that

$$\begin{aligned}\lambda_1' + \mu_1' + \nu_1' + \dots &= \lambda, \\ \lambda_2' + \mu_2' + \nu_2' + \dots &= \mu, \\ \lambda_3' + \mu_3' + \nu_3' + \dots &= \nu;\end{aligned}$$

or, as it is convenient to say, for every separation of the given assemblage of numbers which has the *specification* $\lambda, \mu, \nu \dots$. With this nomenclature we may say that the successive row partitions have a specification $p, q, r \dots$ and we may assert that the lattices under enumeration are associated with a definite assemblage of numbers and with two specifications, all three of which denote partitions of the same number, $\Sigma \lambda' + \Sigma \mu' + \Sigma \nu' + \dots = \lambda + \mu + \nu + \dots = p + q + r + \dots$. We thus associate the lattice with three partitions of one number.

There is a law of symmetry connected with these lattices the true nature of which is not at once manifest; it is *not* obtained by simple transposition of the above lattices, and we are *not* permitted to simply exchange the partitions $(\lambda \mu \nu \dots)$, $(pqr \dots)$ preserving the assemblage of compartment numbers with the object of obtaining identity of enumeration. The difficulty presents itself whenever two or more partitions, $(\lambda_1' \mu_1' \nu_1' \dots)$, $(\lambda_2' \mu_2' \nu_2' \dots)$, &c. \dots are *different* but have the *same specification*. I will obtain the true theorem by the examination of a particular case. Let the assemblage of numbers be 2, 2, 1, 1, and consider the two results

$$(2)^3(1)^2 = \dots + 6(2^3) + \dots$$

Let any operand

$$(\lambda_1' \mu_1' \nu_1' \dots) (\lambda_2' \mu_2' \nu_2' \dots) (\lambda_3' \mu_3' \nu_3' \dots) \dots$$

so multiplied be denoted by

$$\Sigma \text{Co} (\lambda_1' \mu_1' \nu_1' \dots) (\lambda_2' \mu_2' \nu_2' \dots) (\lambda_3' \mu_3' \nu_3' \dots) \dots$$

then we have the following law of symmetry:—

From a given finite assemblage of numbers

$$\lambda_1, \mu_1, \nu_1, \dots, \lambda_2, \mu_2, \nu_2, \dots, \lambda_3, \mu_3, \nu_3, \dots \dots$$

construct all the products

$$(\lambda_1' \mu_1' \nu_1' \dots) (\lambda_2' \mu_2' \nu_2' \dots) (\lambda_3' \mu_3' \nu_3' \dots) \dots$$

which have a given specification $(\lambda \mu \nu \dots)$ and all the products

$$(p_1 q_1 r_1 \dots) (p_2 q_2 r_2 \dots) (p_3 q_3 r_3 \dots) \dots$$

which have a given specification $(pqr \dots)$.

If

$$\Sigma \text{Co} (\lambda_1' \mu_1' \nu_1' \dots) (\lambda_2' \mu_2' \nu_2' \dots) (\lambda_3' \mu_3' \nu_3' \dots) \dots = \dots + A (pqr \dots) + \dots$$

then

$$\Sigma \text{Co} (p_1 q_1 r_1 \dots) (p_2 q_2 r_2 \dots) (p_3 q_3 r_3 \dots) \dots = \dots + A (\lambda \mu \nu \dots) + \dots$$

the lattices being derived from

$$D_{pqr \dots} \Sigma \text{Co} (\lambda_1' \mu_1' \nu_1' \dots) (\lambda_2' \mu_2' \nu_2' \dots) (\lambda_3' \mu_3' \nu_3' \dots) \dots = A$$

$$D_{\lambda \mu \nu \dots} \Sigma \text{Co} (p_1 q_1 r_1 \dots) (p_2 q_2 r_2 \dots) (p_3 q_3 r_3 \dots) \dots = A.$$

This is the most refined law of symmetry that has yet come to light in the algebra of a single system of quantities (*cf.* “Memoirs on Symmetric Functions,” ‘Amer. J.,’ *loc. cit.*). The actual representation of the things enumerated by the number A is obtained with ease by this theory of the lattice.

§ 2.

Art. 8.—So far the operations have been those of the infinitesimal calculus, and the numbers involved in the partitions of the functions have been positive integers excluding zero. If we admit zero as a part in the partitions, we find that we have to do with the operations of the calculus of finite differences. At the commencement of the paper d/dx was shown to be a combinatorial symbol, in that when operating upon a power of x , the said power being positive and integral, it had the effect of summing the results obtained by substituting unity for x in all possible ways in the product of x 's. Now the corresponding operator of the calculus of finite differences,

viz., Δ operates upon a power of x by striking out one x , two x 's, three x 's, &c., in all possible ways and summing the results. Thus

$$\Delta x^3 = \cancel{xxx} + x\cancel{xx} + \cancel{xx}x + \cancel{xxx} + \cancel{xxx} + \cancel{xxx} + \cancel{xxx} = 3x^2 + 3x + 1.$$

This simple fact shows that we may expect a corresponding theory of lattices, and that this is, in fact, the case is seen immediately one introduces the part zero into the partitions of the functions. I have introduced zero parts into partitions in the Memoirs on Symmetric Functions above alluded to, and have imported into the theory the corresponding operators d_0 and D_0 .* It was there shown that, if n be the number of quantities of which the symmetric functions are formed,

$$d_0 = \frac{d}{dn}, \quad D_0 = e^{\frac{d}{dn}} - 1;$$

and thence it appears that we have operations $D_0, d_0, 1 + D_0$ corresponding to the operations $\Delta, d/dn, E$ of the calculus of finite differences.

Considering partitions which only involve zero parts, we have only finite difference operations; if we have other integers, we have mixed operations drawn both from the finite and infinitesimal calculus.

The partition (0^p) is derived from

$$\Sigma \alpha_1^q \alpha_2^q \alpha_3^q \dots \alpha_p^q$$

by putting $q = 0$, and obviously has the value $\binom{n}{p}$ and, in the paper referred to, it has been shown that D_0 operates upon a monomial by erasing one zero part from its partition, so that

$$D_0(0^p) = (0^{p-1}),$$

which is to be compared with the operation of Δ , viz.:—

$$\Delta x^{(m)} = mx^{(m-1)}$$

where $x^{(m)} = x(x-1)(x-2)\dots(x-m+1)$

in the notation of the finite calculus.

Further, it has been shown that D_0 operates upon a product of monomials through its partitions $0, 00, 000, 0000, \dots$ which are infinite in number, viz.:—we are to strike out one zero, two zeros, three zeros, &c., in all possible ways; but in any one such operation not striking out more than one zero from any monomial factor.

$$\begin{aligned} \text{Ex. gr. } D_0(0^3)(0^2)(0) &= (0^2)(0^2)(0) + (0^3)(0)(0) + (0^3)(0^2) \\ &\quad + (0^2)(0)(0) + (0^2)(0^2) + (0^3)(0) \\ &\quad + (0^2)(0) \end{aligned}$$

the successive lines being due to the partitions $0, 00, 000$ respectively.

* 'American Journal of Mathematics,' vol. 12, second memoir, "On a New Theory of Symmetric Functions," p. 71 *et seq.*; and vol. 13, third memoir, &c., pp. 8 *et seq.*

Compare the difference formula

$$\begin{aligned}\Delta u_x v_x w_x &= (EE'E'' - 1) u_x v_x w_x \\ &= (\Delta + \Delta' + \Delta'' + \Delta'\Delta'' + \Delta''\Delta + \Delta\Delta' + \Delta\Delta'\Delta'') u_x v_x w_x,\end{aligned}$$

where u_x is only operated upon by E and Δ , v_x by E' and Δ' , w_x by E'' and Δ'' .

Art. 9.—Consider the lattice theory connected with the operation D_0 and zero-part partition functions.

Take the function

$$(0^\lambda)(0^\mu)(0^\nu) \dots$$

λ, μ, ν, \dots being in descending order; if it be multiplied out, it will appear as a linear function of $(0^\lambda), (0^{\lambda+1}), \dots (0^{\lambda+\mu+\nu+\dots})$, the coefficients being positive (*cf.* Second Memoir, *loc. cit.*, p. 102).

To find therein the coefficient of the term (0^s) we must operate with D_0^s , and the sought coefficient is the resulting *numerical* term. If the factors $(0^\lambda)(0^\mu)(0^\nu) \dots$ be t in number, we are concerned with lattices of t columns and s rows. The first operation of D_0 results in a first row whose compartments contain t or fewer zeros placed in any manner so that not more than one zero is in each compartment; similarly, for the successive rows and the final lattice is subject to the single condition that the numbers of zeros in the successive columns are λ, μ, ν, \dots respectively. The number of such lattices is

$$\{D_0^s(0^\lambda)(0^\mu)(0^\nu) \dots\}_{n=0} = \{(e^{\frac{d}{dn}} - 1)^s \binom{n}{\lambda} \binom{n}{\mu} \binom{n}{\nu} \dots\}_{n=0}$$

or, symbolically,

$$(e^{\frac{d}{do}} - 1)^s \binom{0}{\lambda} \binom{0}{\mu} \binom{0}{\nu} \dots$$

We have thus the analytical solution of a distribution problem upon a lattice.

It may be convenient to give the lattice a literal form by writing a for zero in the compartments.

Art. 10.—Contrast the result obtained with that which arises from

$$D_1^s(1^\lambda)(1^\mu)(1^\nu) \dots$$

The lattices are similar to those above, with the additional condition that each row is to contain but one letter a . Again, from

$$D_{p_1} D_{p_2} \dots D_{p_s}(1^\lambda)(1^\mu)(1^\nu) \dots$$

arise lattices of t columns and s rows with the same condition as the zero lattices, but with the additional conditions that the numbers of letters a in the successive rows are to be p_1, p_2, \dots, p_s respectively. This remark leads to a relationship between the coefficients in the developments of $(1^\lambda)(1^\mu)(1^\nu) \dots$ and $(0^\lambda)(0^\mu)(0^\nu) \dots$ respectively. For let

$$\begin{aligned}(1^\lambda)(1^\mu)(1^\nu) \dots &= \dots + A_{p_1 p_2 \dots p_s} (p_1 p_2 \dots p_s) \\ &\quad + A_{p_1' p_2' \dots p_s'} (p_1' p_2' \dots p_s') + \dots,\end{aligned}$$

the terms written comprising all monomial functions whose partitions contain exactly s parts; and

$$(0^\lambda)(0^\mu)(0^\nu) \dots = \dots + B_s(0^s) + \dots$$

If $P_{p_1 p_2 \dots p_s}$ denote the number of permutations of the numbers p_1, p_2, \dots, p_s , I say that the above lattice theory establishes the relation

$$B_s = P_{p_1 p_2 \dots p_s} A_{p_1 p_2 \dots p_s} + P_{p'_1 p'_2 \dots p'_s} A_{p'_1 p'_2 \dots p'_s} + \dots$$

Ex. gr. Observe the two results

$$\begin{aligned} (1^3)(1)(1) &= (31) + 2(2^2) + 5(21^2) + 12(1^4), \\ (0^3)(0)(0) &= 4(0^2) + 15(0^3) + 12(0^4), \end{aligned}$$

and verify that the relation given obtains between the coefficients.

Art. 11.—This zero theory is really nothing more than a calculus of binomial coefficients, which enables the study of their properties by means of the powerful instruments appertaining to the Theory of Symmetric Functions. The Law of Symmetry established by the author in the Second Memoir (*loc. cit.*) is easily established by means of the lattice; it may be stated in a simple form, because all the functions $(0), (0^2), (0^3), \dots$ are to be regarded as having the same specification, viz. (0) ; further, the specification of $(0^\lambda)(0^\mu)(0^\nu) \dots$ to s factors is (0^s) . Select all the products formed from a *given number* of zeros which have the same specification (0^s) , and attach to each a coefficient equal to the number of permutations of which it is susceptible. Denote the sum of such products by $\Sigma \text{Co } (0^\lambda)(0^\mu)(0^\nu) \dots$. Similarly, for a specification (0^s) denote the sum of such products by $\Sigma \text{Co } (0^p)(0^q)(0^r) \dots$. Then

$$\begin{aligned} \Sigma \text{Co } (0^\lambda)(0^\mu)(0^\nu) \dots &= \dots + A(0^s) + \dots \\ \Sigma \text{Co } (0^p)(0^q)(0^r) \dots &= \dots + A(0^s) + \dots \end{aligned}$$

the coefficient A being the same in both cases.

Ex. gr. Verify that

$$\begin{aligned} 2(0^3)(0) + (0^2)^3 &= \dots + 12(0^3) + \dots \\ 3(0^2)(0)^2 &= \dots + 12(0^2) + \dots \end{aligned}$$

§ 3.

Art. 12.—I continue the general plan of this paper, viz. :—I do not attempt the solution of any particular problems, unless they are suggested by the general course of the investigation, but rather start with definite operations and functions, and seek to discover the problems of which they furnish the solution. This is the reverse process to that employed in the 'Trans. Camb. Phil. Soc.' (*loc. cit.*), where I particularly investigated a number of questions more or less directly associated with

the famous Problem of the Latin Square. I anticipate what follows to the extent of observing that the Latin Square again presents itself without special effort on the part of the investigator, and that a new and very simple solution of that and associated problems is obtained.

I seek to obtain theorems which flow from a consideration of symmetric functions of several systems of quantities, taken in conjunction with appropriate operations.

I make the reference MACMAHON, "Memoir on the Roots of Systems of Equations," 'Phil. Trans.,' A, 1890.

Consider the systems of quantities

$$\begin{aligned} \alpha_1, \alpha_2, \alpha_3, \dots \\ \beta_1, \beta_2, \beta_3, \dots \\ \gamma_1, \gamma_2, \gamma_3, \dots \\ \dots \end{aligned}$$

and write

$$\begin{aligned} (1 + \alpha_1 x_1 + \beta_1 x_2 + \gamma_1 x_3 + \dots)(1 + \alpha_2 x_1 + \beta_2 x_2 + \gamma_2 x_3) \dots \\ = 1 + \alpha_{100} \dots x_1 + \alpha_{010} \dots x_2 + \dots + \alpha_{pqr} \dots x_1^p x_2^q x_3^r \dots + \dots \end{aligned}$$

Denote the symmetric function

$$\Sigma \alpha_1^{p_1} \beta_1^{q_1} \gamma_1^{r_1} \dots \alpha_2^{p_2} \beta_2^{q_2} \gamma_2^{r_2} \dots \alpha_3^{p_3} \beta_3^{q_3} \gamma_3^{r_3} \dots$$

by

$$(p_1 q_1 r_1 \dots p_2 q_2 r_2 \dots p_3 q_3 r_3 \dots)$$

so that

$$\alpha_{pqr} \dots = (\overline{100 \dots}^p \overline{010 \dots}^q \overline{001 \dots}^r \dots)$$

Ex. gr.

$$\alpha_{1111} = \Sigma \alpha_1 \beta_2 \gamma_3 \delta_4 = (\overline{1000} \overline{0100} \overline{0010} \overline{0001})$$

The quantities $\alpha_{pqr} \dots$ are the elementary symmetric functions.

The linear operator $d_{\pi\kappa\rho} \dots$ is defined by

$$d_{\pi\kappa\rho} \dots = \Sigma^{p,q,r,\dots} a_{p-\pi, q-\kappa, r-\rho, \dots} \frac{d}{da_{pqr} \dots},$$

so that

$$d_{100} \dots = \Sigma a_{p-1, q, r, \dots} \frac{d}{da_{pqr} \dots},$$

$$d_{010} \dots = \Sigma a_{p, q-1, r, \dots} \frac{d}{da_{pqr} \dots},$$

$$d_{001} \dots = \Sigma a_{p, q, r-1, \dots} \frac{d}{da_{pqr} \dots},$$

and then

$$D_{pqr} \dots = \frac{1}{p!q!r! \dots} d_{100} \dots d_{010} \dots d_{001} \dots,$$

the multiplication of operators being symbolic as in TAYLOR'S theorem, so that $D_{pqr} \dots$ is an operator of the order $p + q + r + \dots$ and does not denote

$p + q + r + \dots$ successive linear operations. The operation of $D_{pqr} \dots$ upon a monomial symmetric function has been explained (*loc. cit.*). It has the effect of obliterating a part $\overline{pqr} \dots$ from the partition of the function when such a part is present, and an annihilating effect in every other case. The operation upon a product has the effect of erasing a partition of $\overline{pqr} \dots$ from the product, one part from each factor in all possible ways, the result of the operation being a sum of products, one product arising from each erasure of a partition.

Ex. gr. $D_{43}(\overline{43} \ 22) = (\overline{22}).$

If we have to operate with D_{43} upon

$$(\overline{32} \ \overline{22}) (\overline{21} \ \overline{11})$$

we have to erase the two partitions $(\overline{32} \ \overline{11})$, $(\overline{22} \ \overline{21})$, and arrive at

$$D_{43}(\overline{32} \ \overline{22}) (\overline{21} \ \overline{11}) = (\overline{22}) (\overline{21}) + (\overline{32} \ \overline{11}).$$

Art. 13.—It will suffice to consider three systems of quantities as typical of the general case.

Take the function

$$a_{\lambda_1 \mu_1 \nu_1} a_{\lambda_2 \mu_2 \nu_2} \dots a_{\lambda_s \mu_s \nu_s} = (\overline{100}^{\lambda_1} \overline{010}^{\mu_1} \overline{001}^{\nu_1}) (\overline{100}^{\lambda_2} \overline{010}^{\mu_2} \overline{001}^{\nu_2}) \dots (\overline{100}^{\lambda_s} \overline{010}^{\mu_s} \overline{001}^{\nu_s})$$

and the operation

$$D_{p_1 q_1 r_1} D_{p_2 q_2 r_2} \dots D_{p_t q_t r_t}$$

$$(\overline{\lambda_1 \mu_1 \nu_1} \ \overline{\lambda_2 \mu_2 \nu_2} \dots \overline{\lambda_s \mu_s \nu_s}) \text{ and } (\overline{p_1 q_1 r_1} \ \overline{p_2 q_2 r_2} \dots \overline{p_t q_t r_t})$$

being each partitions of the same tripartite number.

$$\text{If } a_{\lambda_1 \mu_1 \nu_1} a_{\lambda_2 \mu_2 \nu_2} \dots a_{\lambda_s \mu_s \nu_s} = \dots + A(p_1 q_1 r_1 p_2 q_2 r_2 \dots p_t q_t r_t) + \dots, \\ D_{p_1 q_1 r_1} D_{p_2 q_2 r_2} \dots D_{p_t q_t r_t} a_{\lambda_1 \mu_1 \nu_1} a_{\lambda_2 \mu_2 \nu_2} \dots a_{\lambda_s \mu_s \nu_s} = A;$$

and we have to determine the nature of the lattices enumerated by the number A. The tripartite number $(\overline{p_1 q_1 r_1})$ has a partition of $p_1 + q_1 + r_1$ parts, viz.:— $\overline{100}^{p_1} \overline{010}^{q_1} \overline{001}^{r_1}$ so that, in operating with $D_{p_1 q_1 r_1}$ upon the operand, we have to select this partition from the product, one part from each factor, in all possible ways; the operation breaks up into minor operations as usual, and the first row of the lattice of s columns and t rows will contain in $p_1 + q_1 + r_1$ of its compartments the tripartite numbers 100, 010, 001 (p_1 of the first, q_1 of the second, and r_1 of the third) in some order; the assemblage of numbers in this row is the partition of the elementary function $a_{p_1 q_1 r_1}$. Similarly a minor operation of $D_{p_2 q_2 r_2}$ produces a second row containing tripartite numbers, the assemblage of which constitutes the elementary function $a_{p_2 q_2 r_2}$. We finally arrive at a lattice such that the tripartites in the successive rows constitute the elementary functions $a_{p_1 q_1 r_1}, a_{p_2 q_2 r_2}, \dots a_{p_t q_t r_t}$ respec-

tively, and in the successive columns the elementary functions $a_{\lambda_1\mu_1\nu_1}, a_{\lambda_2\mu_2\nu_2}, \dots, a_{\lambda_s\mu_s\nu_s}$, respectively, and the number A enumerates the lattices possessing this property.

We may give this case a purely literal form by writing $100 = a, 010 = b, 001 = c$, and then we have a lattice of s columns and t rows, such that the products of letters in the successive rows are $a^{p_1}b^{q_1}c^{r_1}, a^{p_2}b^{q_2}c^{r_2}, \dots, a^{p_t}b^{q_t}c^{r_t}$ respectively, and in the successive columns $a^{\lambda_1}b^{\mu_1}c^{\nu_1}, a^{\lambda_2}b^{\mu_2}c^{\nu_2}, \dots, a^{\lambda_s}b^{\mu_s}c^{\nu_s}$ respectively.

Art. 14.—Stated in this form the problem appears to have a close relationship to the problem of the Latin Square. It is in fact a new generalization of that problem; for put $s = t = 3$ and

$$p_1 = q_1 = r_1 = p_2 = q_2 = r_2 = p_3 = q_3 = r_3 = 1$$

$$\lambda_1 = \mu_1 = \nu_1 = \lambda_2 = \mu_2 = \nu_2 = \lambda_3 = \mu_3 = \nu_3 = 1$$

so that the operation is D_{in}^3 and the function α_{in}^3 . One lattice is then

010	100	001
001	010	100
100	001	010

or in literal form

b	a	c
c	b	a
a	c	b

which is a Latin Square. Hence the numbers of Latin Squares of order 3 is

$$D_{\text{in}}^3 \alpha_{\text{in}}^3,$$

and in general of order n

$$D_{\text{in} \dots 1}^n \alpha_{\text{in} \dots 1}^n,$$

a very simple solution of the problem. If reference be made to the solution arrived at (*loc. cit.*) by considerations relating to a single system of quantities, it will be noticed that the peculiar difficulties intrinsically present in that solution disappear at once when n systems of quantities are brought in as auxiliaries. The Latin Square appears at the outset of this investigation, and in a perfectly natural manner.

Art. 15.—Now put

$$p_1 = p_2 = \dots = p_{\lambda+\mu+\nu} = \lambda = \lambda_1 = \lambda_2 = \dots = \lambda_{\lambda+\mu+\nu}$$

$$q_1 = q_2 = \dots = q_{\lambda+\mu+\nu} = \mu = \mu_1 = \mu_2 = \dots = \mu_{\lambda+\mu+\nu}$$

$$r_1 = r_2 = \dots = r_{\lambda+\mu+\nu} = \nu = \nu_1 = \nu_2 = \dots = \nu_{\lambda+\mu+\nu}$$

so that $s = t = \lambda + \mu + \nu$. We have then lattices enumerated by

$$D_{\lambda\mu\nu}^{\lambda+\mu+\nu} \alpha_{\lambda\mu\nu}^{\lambda+\mu+\nu},$$

and, in the literal form, they are such that the product of letters in each of the $\lambda + \mu + \nu$ rows and $\lambda + \mu + \nu$ columns is $a^\lambda b^\mu c^\nu$, one letter appearing in each compartment of the lattice. This is the extension of the idea of the Latin Square which was successfully considered in the former paper (*loc. cit.*), but now the enumeration is given in a simpler form and from simpler considerations.

In general, it has been established above that the Latin Squares based upon the product

$$a^\lambda b^\mu c^\nu \dots$$

are enumerated by the expression

$$D_{\lambda\mu\nu\dots}^{\lambda+\mu+\nu+\dots} \quad \alpha_{\lambda\mu\nu\dots}^{\lambda+\mu+\nu+\dots}$$

the simplicity of which leaves nothing to be desired.

Art. 16.—Consider the particular case of the general theorem which is such that no compartment is empty; the lattice has n columns and m rows.

$$\begin{aligned} p_1 + q_1 + r_1 &= p_2 + q_2 + r_2 = \dots = p_m + q_m + r_m = n \\ \lambda_1 + \mu_1 + \nu_1 &= \lambda_2 + \mu_2 + \nu_2 = \dots = \lambda_n + \mu_n + \nu_n = m, \end{aligned}$$

the corresponding lattices being enumerated by

$$D_{p_1 q_1 r_1} D_{p_2 q_2 r_2} \dots D_{p_m q_m r_m} \quad \alpha_{\lambda_1 \mu_1 \nu_1} \alpha_{\lambda_2 \mu_2 \nu_2} \dots \alpha_{\lambda_n \mu_n \nu_n}$$

These, when given the literal form, possess the property that the products of letters in the successive rows are $a^{p_1} b^{q_1} c^{r_1}$, $a^{p_2} b^{q_2} c^{r_2}$, \dots , $a^{p_m} b^{q_m} c^{r_m}$ respectively, and in the successive columns $a^{\lambda_1} b^{\mu_1} c^{\nu_1}$, $a^{\lambda_2} b^{\mu_2} c^{\nu_2}$, \dots , $a^{\lambda_n} b^{\mu_n} c^{\nu_n}$ respectively.

Ex. gr. Suppose the row products to be $a^3 b$, $a^2 b^2$, $a^2 b^2$, a^4 , and the column products a^4 , $a^3 b$, $a^3 b$, ab^3

$$\begin{aligned} & D_{31} D_{22} D_{40} a_{40} a_{31} a_{18} \\ &= D_{31} D_{22} D_{40} (\overline{10}^4) (\overline{10}^3 \overline{01})^2 (\overline{10} \overline{01}^3) \\ &= D_{31} D_{22} (\overline{10}^3) (\overline{10}^2 \overline{01})^2 (\overline{01}^3) \\ &= D_{22}^2 (\overline{10}^2) (\overline{10} \overline{01})^2 (\overline{01}^2) \\ &= D_{22} 2(\overline{10})^2 (\overline{01})^3 \\ &= 2. \end{aligned}$$

and the two lattices are

a	a	a	b
a	a	b	b
a	b	a	b
a	a	a	a

a	a	a	b
a	b	a	b
a	a	b	b
a	a	a	a

Again, suppose the row products to be a^3b , a^2b^2 , a^2b^3 , and the column products a^3 , a^2b , a^2b , b^3

$$\begin{aligned} & D_{31}D_{22}^2 a_{30} a_{21}^2 a_{03} \\ &= D_{31}D_{22}^2 (\overline{10^3})(\overline{10^2 \overline{01}})^2 (\overline{01^2}) \\ &= D_{22}^2 (\overline{10^2})(\overline{10 \overline{01}})^2 (\overline{01^2}) \\ &= 2D_{22}(\overline{10})^2 (\overline{01})^2 = 2, \end{aligned}$$

and the lattices are

<i>a</i>	<i>a</i>	<i>a</i>	<i>b</i>
<i>a</i>	<i>a</i>	<i>b</i>	<i>b</i>
<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>

<i>a</i>	<i>a</i>	<i>a</i>	<i>b</i>
<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
<i>a</i>	<i>a</i>	<i>b</i>	<i>b</i>

Art. 17.—In general, we may state that the lettered lattices, which are such that the row products are in order

$$\alpha^{p_1} b^{q_1} c^{r_1} \dots k^{z_1}, \alpha^{p_2} b^{q_2} c^{r_2} \dots k^{z_2}, \dots \alpha^{p_m} b^{q_m} c^{r_m} \dots k^{z_m},$$

and the column products in order

$$\alpha^{\lambda_1} b^{\mu_1} c^{\nu_1} \dots k^{\zeta_1}, \alpha^{\lambda_2} b^{\mu_2} c^{\nu_2} \dots k^{\zeta_2}, \dots \alpha^{\lambda_n} b^{\mu_n} c^{\nu_n} \dots k^{\zeta_n},$$

one letter being in each compartment, are enumerated by

$$D_{p_1 q_1 r_1} \dots z_1 D_{p_2 q_2 r_2} \dots z_2 \dots D_{p_m q_m r_m} \dots z_m \alpha_{\lambda_1 \mu_1 \nu_1} \dots \zeta_1 \alpha_{\lambda_2 \mu_2 \nu_2} \dots \zeta_2 \dots \alpha_{\lambda_n \mu_n \nu_n} \dots \zeta_n;$$

a very interesting development of the Latin Square problem.

We have found above the nature of the lattices enumerated by the number

$$D_{p_1 q_1 r_1} \dots D_{p_2 q_2 r_2} \dots \dots D_{p_i q_i r_i} \dots \alpha_{\lambda_1 \mu_1 \nu_1} \dots \alpha_{\lambda_2 \mu_2 \nu_2} \dots \dots \alpha_{\lambda_n \mu_n \nu_n} \dots$$

any number of systems of quantities being involved, and the mere fact of the existence of the lattices indicates a law of symmetry which may be stated as follows:—

If

$$\alpha_{\lambda_1 \mu_1 \nu_1} \dots \alpha_{\lambda_2 \mu_2 \nu_2} \dots \dots \alpha_{\lambda_i \mu_i \nu_i} \dots = \dots + A(\overline{p_1 q_1 r_1} \dots \overline{p_2 q_2 r_2} \dots \dots \overline{p_i q_i r_i} \dots) + \dots$$

then

$$\alpha_{p_1 q_1 r_1} \dots \alpha_{p_2 q_2 r_2} \dots \dots \alpha_{p_i q_i r_i} \dots = \dots + A(\overline{\lambda_1 \mu_1 \nu_1} \dots \overline{\lambda_2 \mu_2 \nu_2} \dots \dots \overline{\lambda_i \mu_i \nu_i} \dots) + \dots$$

Art. 18.—The next case that comes forward for examination is that connected with the homogeneous product sums $h_{\lambda \mu \nu} \dots$. We require the theorem

$$D_{pqr} \dots h_{\lambda \mu \nu} \dots = h_{\lambda - p, \mu - q, \nu - r} \dots$$

and also

$$D_{pqr} \dots h_{\lambda_1 \mu_1 \nu_1} \dots h_{\lambda_2 \mu_2 \nu_2} \dots \dots h_{\lambda_s \mu_s \nu_s} \dots \\ = \Sigma h_{\lambda_1 - p_1, \mu_1 - q_1, \nu_1 - r_1} \dots h_{\lambda_2 - p_2, \mu_2 - q_2, \nu_2 - r_2} \dots \dots h_{\lambda_s - p_s, \mu_s - q_s, \nu_s - r_s} \dots$$

where $(\overline{p_1 q_1 r_1} \dots \overline{p_2 q_2 r_2} \dots \dots \overline{p_s q_s r_s} \dots)$ is a partition of $(\overline{pqr} \dots)$, and the sum is for all such partitions and for a particular partition is for all ways of operating upon the suffixes with the parts of the partition. *Ex. gr.*

$$D_{11} h_{11} h_{22} = h_{22} + h_{11}^2 + h_{01} h_{21} + h_{10} h_{12}$$

Taking only tripartite functions for convenience, consider the function

$$h_{\lambda_1 \mu_1 \nu_1} h_{\lambda_2 \mu_2 \nu_2} \dots h_{\lambda_s \mu_s \nu_s}$$

and the operation

$$D_{p_1 q_1 r_1} D_{p_2 q_2 r_2} \dots D_{p_t q_t r_t};$$

we have

$$D_{p_1 q_1 r_1} D_{p_2 q_2 r_2} \dots D_{p_t q_t r_t} h_{\lambda_1 \mu_1 \nu_1} h_{\lambda_2 \mu_2 \nu_2} \dots h_{\lambda_s \mu_s \nu_s} = A;$$

where

$$(\overline{p_1 q_1 r_1} \overline{p_2 q_2 r_2} \dots \overline{p_t q_t r_t}) \text{ and } (\overline{\lambda_1 \mu_1 \nu_1} \overline{\lambda_2 \mu_2 \nu_2} \dots \overline{\lambda_s \mu_s \nu_s})$$

being partitions of the same tripartite number,

$$h_{\lambda_1 \mu_1 \nu_1} h_{\lambda_2 \mu_2 \nu_2} \dots h_{\lambda_s \mu_s \nu_s} = \dots + A(\overline{p_1 q_1 r_1} \overline{p_2 q_2 r_2} \dots \overline{p_t q_t r_t}) + \dots$$

The operation of $D_{p_1 q_1 r_1}$ upon the product splits up as usual into a number of minor operations, one of which, as shown above, is connected with one of its partitions operating in a definite manner upon the suffixes $\lambda_1 \mu_1 \nu_1, \lambda_2 \mu_2 \nu_2, \dots, \lambda_s \mu_s \nu_s$. Hence the first row of the lattice has in certain of its s compartments the tripartite parts of some partition of $\overline{p_1 q_1 r_1}$; the second row also will have in certain of its compartments the tripartite parts of some partition of $\overline{p_2 q_2 r_2}$; and finally we must arrive at a lattice whose rows are associated with partitions of $\overline{p_1 q_1 r_1}, \overline{p_2 q_2 r_2}, \dots, \overline{p_t q_t r_t}$ respectively, and whose t columns are associated with partitions of $\overline{\lambda_1 \mu_1 \nu_1}, \overline{\lambda_2 \mu_2 \nu_2}, \dots, \overline{\lambda_s \mu_s \nu_s}$ respectively. There is no restriction on the magnitude of the constituents of the various tripartite numbers which appear in the compartments. The lattices thus defined are enumerated by the number A . We may give the lattice a literal form by writing $a^\rho b^\sigma c^\tau$ for $(\rho\sigma\tau)$ in a compartment. We then have a theorem which may be stated as follows:—

Monomial products of letters a, b, c, \dots may be placed in the compartments of a lattice of t rows and s columns in such wise that the multiplication of products in successive rows produces $a^{\rho_1} b^{\sigma_1} c^{\tau_1} \dots, a^{\rho_2} b^{\sigma_2} c^{\tau_2} \dots, \dots, a^{\rho_t} b^{\sigma_t} c^{\tau_t} \dots$ respectively, and in successive columns produces $a^{\lambda_1} b^{\mu_1} c^{\nu_1} \dots, a^{\lambda_2} b^{\mu_2} c^{\nu_2} \dots, \dots, a^{\lambda_s} b^{\mu_s} c^{\nu_s} \dots$ respectively in a number of ways enumerated by the number A above defined.

It is scarcely necessary to observe that

$$\Sigma \rho - \Sigma \lambda = \Sigma q - \Sigma \mu = \Sigma r - \Sigma \nu = \dots = 0,$$

and that only $s + t - 1$ of the $s + t$ literal products are independent.

Art. 19.—In conclusion, it may be remarked that there is no difficulty in evolving a mixed theory which involves the operation both of the infinitesimal calculus and of the finite calculus. Operations and functions may be designed which lead to lattices which are not rectangular. The theory may be connected with complete or incomplete lattices in three or more dimensions; and finally one of the most promising paths of research appears to be connected with a multipartite zero. These matters may be the subjects of future investigation. For the present enough has been said to indicate the apparent scope of the new method.

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